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Recent studies on iron meteorites. I

Introduction

F. A. Paneth

Londonderry Laboratory for Radiochemistry, University of Durham

ABSTRACT

The connection is indicated between the previous investigations on iron meteorites and the recent studies carried out in this laboratory.

About a quarter of a century ago methods were developed for the handling of rare gases—especially helium—which permitted the measurement of considerably smaller quantities than had been dealt with before. They were first applied to the investigation of elementary transmutations, but it was obvious that they also opened up approaches to the study of other problems which had been inaccessible so far [19]. One of them was the age determination by the "helium method" for natural materials of very low radioactivity; it now became possible to use, instead of uranium and thorium minerals, any rocks or meteorites. Especially the study of the latter group [2] seemed interesting as—contrary to the case of terrestrial rocks—no other source of information about the geological age of meteorites was obtainable and any progress in this direction was likely to help in the solution of the obscure question of their origin [12].

It soon became obvious, however, that one could not hope to achieve reliable age data unless the measurement not only of the helium accumulated in meteorites, but also that of their uranium and thorium content could be improved. Stone meteorites contain smaller quantities of these two elements than even ultra-basic terrestrial rocks, and iron meteorites are still less "contaminated" by these radioactive substances, as can be seen from the following Table I of average values [14]. The methods known for the determination of uranium and thorium proved to be

Table 1. *Average uranium and thorium content of rocks and meteorites* (*in* 10^{-6} *g per g*)

	Uranium	*Thorium*
Acidic igneous rocks	4·1	13·0
Basic igneous rocks	1·1	3·9
Stone meteorites	0·35	1·0
Iron meteorites	0·007	0·04

unreliable if applied to such micro-quantities and we were forced to attempt their refinement [9] after having achieved that of the helium measurements. From 1927 on, practically every improvement in the technique of radioactive measurements leading to higher sensitivity was tentatively applied by us to the determination of the uranium and thorium content of meteorites. Progress was slow,

partly owing to external circumstances, and it was only in 1942 that we could offer with confidence figures for the uranium and thorium, as well as the helium, content of six iron meteorites [13]. Throughout these years we concentrated our efforts almost exclusively on irons since stones cannot be relied upon to be helium tight, and the best analytical results are therefore of doubtful value if used for the calculation of their geological ages. The fundamental difference in the helium-tightness of iron and stone meteorites can be seen from Fig. 1 which shows the percentage of helium released if the meteorites were heated at increasing temperatures for periods of three hours at each stage [11].

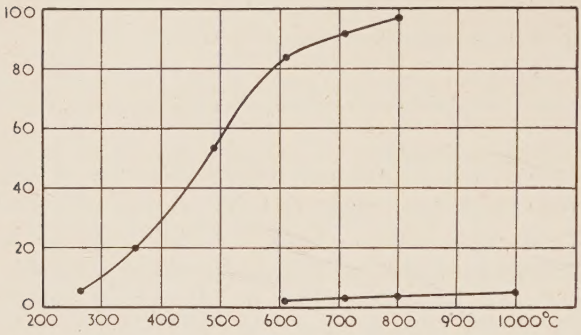

Fig. 1. Percentage loss of Helium (3 hours heating at each stage).
Upper curve: Stone meteorite Pultusk.
Lower curve: Iron meteorite Mount Ayliff.

The uranium figures presented in our 1942 paper were considerably lower than those found earlier in other laboratories and by ourselves; they were confirmed independently [20] in 1950, and our recent studies have also shown their essential reliability. No other laboratory has so far measured the thorium content of iron meteorites. Owing to the pressure of other occupations in 1942, the results of our work were published only briefly, with little more than a few remarks about the techniques by which they had been obtained. It was our intention to give a full account of the experimental procedure later, but, when we were able to return to the meteorite work, methods for sensitive radioactive measurements had been developed which we hoped would be more satisfactory than those applied by us in pre-war days, and we had also—thanks to the foundation in Durham of a special laboratory for radiochemistry—greater means at our disposal. We resumed our investigations on a larger basis, and to-day it seems hardly any longer worth while to put into print details of the work which led to the 1942 results, as in almost every direction some progress has been made in the experimental procedures. As far as the helium measurements are concerned, the changes consist mainly in refinements of the old technique which enable us now to obtain accurate results on fractions of a gram of the meteorite material. The principles of the uranium and thorium analyses, however, have been completely altered. In the years 1926–1933 we used two ionization chambers in a differential circuit, with visual observation [9]. Between 1935 and 1942 we counted single disintegrations by a photographic method [13]. From 1947 on we employed amplifiers and automatic counters. In all these arrangements we did not measure directly uranium or thorium, but the equilibrium quantities of radon and thoron which were introduced into the ionization chambers. Radon was in some instances collected directly from the meteorite [13], but usually we allowed radon and thoron to grow from radium and thorium X, respectively, precipitated with barium sulphate out of the meteorite solution. Recently we have started the direct determination of uranium by a

fluorescence method, and are determining thorium by measuring the equilibrium quantity of thorium C, using a scintillation counter. These new methods have the advantages of greater simplicity, speed and reliability, and are applicable to smaller quantities of material, although for a uranium analysis we still need about ten grams, for a thorium analysis forty grams of an average iron meteorite.

It may be of some interest to give here the number of atoms of uranium, radium and radon, thorium, thorium X, thoron and thorium C which have to be dealt with in meteorite analyses (Table 2). They will help to explain the difficulties encountered.

The new methods did not reveal any serious errors in our previous results. On the other hand, the interpretation of these results had now to take into consideration the advances made in the mean time in the study of the effects of

Table 2. Quantities contained in 1 g of an iron meteorite.

	Grammes	*Atoms*
Uranium	$0{\cdot}7 \times 10^{-8}$	$1{\cdot}8 \times 10^{13}$
Radium	$2{\cdot}4 \times 10^{-15}$	$6{\cdot}2 \times 10^{6}$
Radon	$1{\cdot}5 \times 10^{-20}$	4×10
Thorium	4×10^{-8}	1×10^{14}
Thorium X	$2{\cdot}2 \times 10^{-20}$	6×10
Thoron	$3{\cdot}8 \times 10^{-24}$	1×10^{-2}
Thorium C	$2{\cdot}5 \times 10^{-22}$	$6{\cdot}5 \times 10^{-1}$
Helium	$<2 \times 10^{-10}$ to 4×10^{-5} cc	
	$<4 \times 10^{-14}$ to 8×10^{-9} g	
	$<5 \times 10^{9}$ to 1×10^{15} atoms	

cosmic rays on matter which, as is known to-day, may produce some helium; this helium, not being a disintegration product of the uranium and thorium content of the meteorites, has to be neglected in the formulae on which the radioactive age calculations are based. This was first pointed out by Bauer [21] and by Huntley [22] as a likely source of error in our previous calculations. We have tested this hypothesis in two ways: by determining the isotopic composition of the helium present in iron meteorites [18], and by studying its quantity in dependence on the distance from the surface of the meteorite. We found that in some meteorites a substantial part of the helium content owes its formation to cosmic rays.

For readers, who want to obtain more information about the gradual development of our experimental methods and accumulation of results than is contained in this introduction to the recent studies; we append a chronological list of references (Nos. 1 to 19). In the two papers which follow, my collaborators are describing the methods which, during the last few years, they have developed and used for the measurement of helium, uranium and thorium in meteorites. Those of our previous results which we still consider reliable are added for easier reference.

The last paper deals with the problem of the production of helium by cosmic rays, and attempts to calculate their ages on the basis of our present knowledge.

We wish to express our gratitude to *Imperial Chemical Industries, Ltd.*, who have generously made available to us a large part of the specialized equipment needed for this work.

For presenting us with samples of the North Chilean Hexahedrites we are indebted to Mr. E. P. Henderson of the Smithsonian Institute, Washington (D.C.); for samples of Serrania de Varas, Toluca, Sacramenta Mountains and Thunda to Dr. Campbell Smith and Dr. M. H. Hey of the British Museum (Natural History); for the Treysa drillings to Dr. E. Hellner of the Mineralogical Institute of the University of Marburg a.d. Lahn; for a sample of Muonionalusta I to Professor Helge Backlund (Upsala), of Muonionalusta II to Professor F. E. Wickman (Stockholm); for a sample of Cape York (Savik) to Dr. K. Callison (Copenhagen); for a sample and drillings of Carbo and a sample of Bethany to Dr. C. Frondel (Harvard).

We had the privilege of discussing our problems with colleagues in other Universities whose valuable help is gratefully acknowledged in the appropriate places.

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Recent studies on iron meteorites. II

Determination of the helium content

K. F. Chackett, P. Reasbeck and E. J. Wilson

Londonderry Laboratory for Radiochemistry, University of Durham

(*Received* 11 *April* 1953)

ABSTRACT

The experimental technique for the determination of helium in iron meteorites is described in detail. Results are tabulated, and a short discussion of their reliability and significance is given.

Introduction

As has already been pointed out (see Part I), the helium contained in solid iron meteorites is quite unable to escape, but it may do so, with some difficulty, if the iron is molten. A better method of extracting the helium into the gaseous phase is by solution of the material in suitable aqueous reagents which may then be degassed by conventional methods. This is the procedure we have adopted. If one gram of an iron meteorite is dissolved in acid, 400 cc of hydrogen are evolved. The helium present may be only of the order of 2×10^{-7} cc or less; thus the helium to be measured will be diluted by up to 2×10^{9} times its amount of hydrogen, and a large experimental problem is the removal of this hydrogen without loss of helium.

We have also worked with a black chondrite (Beddgelert) from the stony part of which the helium was released by repeated fusion with potassium hydroxide. We describe below these extraction procedures in detail, and then the method of analysis of the evolved gases.

An essential preliminary to all work of this nature is the attainment of really high vacua, not too easy a task with such a complicated system. We have found it best to use a pair of well designed *Pyrex* mercury vapour pumps with liquid air traps, backed by a *Speedivac* oil rotary pump. We have not measured the absolute value of the limiting pressure attainable by this combination but it must be very low as we have observed the mercury to "stick" in the closed limb of a McLeod gauge having an 800 cc bulb while the mercury in the open limb was pulled down 15 or 20 cm from a level just above the top of the closed limb.

Extraction Procedures for Helium

A. Solution of iron meteorites in acid

A very convenient reagent for the solution of iron meteorites is dilute sulphuric acid saturated with potassium persulphate. This has the advantages of being easily purified from atmospheric gases by electrolysis between platinum electrodes, of acting rapidly, and of introducing no radioactive contaminants. The latter point was important in the cases in which we wished to make analyses for helium, uranium, and thorium in one and the same sample. It has the disadvantage that when large quantities of meteorite are to be dissolved, the volume of hydrogen is

correspondingly large, but this is overcome by controlled burning of the hydrogen with a slight excess of oxygen in a special chamber designed to minimise the risk of explosion (a development of a method first used in other connections) [1].

Normally, however, since our helium apparatus is so sensitive, it is necessary to use only 20–200 mg of meteorite, preferably in the form of saw-dust. This is weighed out into the small glass bucket *B* and the apparatus assembled as in Fig. 1 with 30 cc of 5*N* sulphuric acid saturated with potassium persulphate in the dissolving vessel. The acid is freed from dissolved air by electrolysis using the two platinum wires projecting into it as electrodes, the electrolytic gas being pumped away via *E*. Usually 30 minutes of electrolysis is sufficient; a good method was found to be to pass current with *E* closed until 5 cm pressure could be read on the manometer *C*, then pumping away with *E* open for 10 seconds or so, and repeating six or eight times. Finally the lead to vacuum is closed and the saw-dust lowered into the acid by moving along the iron slug *A* with an external magnet. As the quantity of meteoritic material is small, solution occurs within about an hour. The hydrogen liberated is burnt with oxygen (see below) which is led into the vessel via the mercury bubbler *D*; it is general practice to arrange always to have oxygen present in excess. Ignition is started by means of the electrically heated spiral.

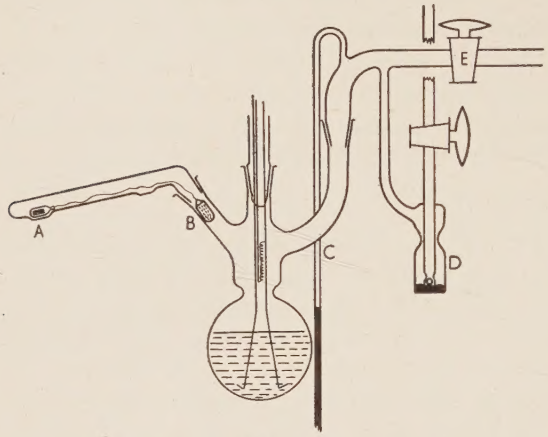

Fig. 1.

B. Solution of iron meteorites in potassium cuprichloride solution

For the $^3He/^4He$ ratio determinations, amounts of helium of the order of 10^{-4} ccs are required so that much larger quantities of meteorites have to be dissolved, generally 10–15 g and in order to avoid the production of large volumes of hydrogen by acid dissolution, potassium cupri-chloride solution is used [2]. The usual mixture is: 43 g $CuCl_2$, 37 g KCl and 18 cc conc. HCl made up to 200 cc with distilled water. The dissolving vessel is similar in arrangement to that shown in Fig. 1, except that it is much larger and the flushing to free the reagent from dissolved air is done by bubbling pure O_2 through the solution instead of using electrolytic gas, as the latter method would generate troublesome amounts of chlorine. This method of dissolution is not used where it is necessary to do a uranium and thorium determination as well, since it is extremely difficult to obtain this reagent sufficiently free from radioactive contaminants.

C. Fusion of stone meteorite with potassium hydroxide

In addition to the iron meteorites we have worked on a stone (Beddgelert). In order to obtain helium from this, the coarsely powdered material is weighed out

into the platinum crucible (Fig. 2) which already contains about half a gram of potassium hydroxide which has previously been melted and allowed to cool in vacuum. The platinum furnace is then attached to the main apparatus, using wax, at the same standard joint as was used for the dissolving vessel for metallic samples. Helium is then driven out of the stone by heating to about 800°C, the

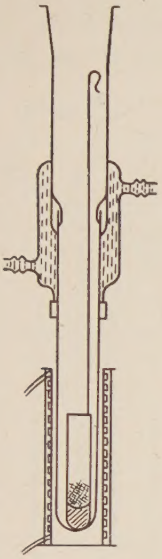

Fig. 2.

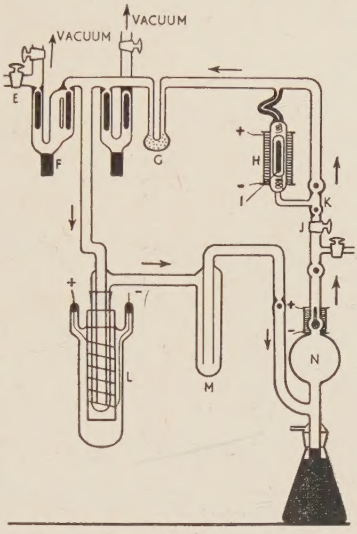

Fig. 3.

waxed joint being kept cold by the water jacket below it. Several heatings are carried out with helium measurements between each to ensure that all the helium is released.

Analysis of evolved gases

The rest of the procedure is as follows, either for iron or stone samples. The mercury in the ventil *F* (Fig. 3) is adjusted so that the two limbs are only just cut off and the charcoal in the U-tube *G* is cooled in liquid nitrogen. A pressure of 2 cm of pure oxygen is admitted to the dissolving vessel or the platinum furnace, whichever is used, and the tap *E* opened cautiously. When the mercury in *F* has stopped bubbling, *E* is shut and the process repeated five more times. In this way all the helium is swept beyond *F* into the next section of the apparatus, although of course it will condense only to a very small extent into the trap *G*. Finally the ventil *F* is fully closed; it will be noted that this ventil is never completely opened, so that it acts as a non-return valve.

The trap *G* is then warmed up to room temperature again and the circulating pump *H* is switched on. It will be seen from the diagram that the reciprocating action of the plunger *I* will cause circulation of the gas in the part of the apparatus indicated by the arrows, the tap *J* being open, thanks to the valve action of the two ground-in steel balls at *K*. This reciprocating motion is achieved by periodic excitation of the solenoid by means of an electric motor and a cam-operated

switch (not shown). The gas circulates in turn through a heated glass tube L containing palladium black and surrounded by a water-cooled jacket, and a water vapour trap M. Circulation for 30 minutes is normally carried out; this removes the last traces of hydrogen from the gas. The technique described here replaces the earlier one of absorbing hydrogen in heated calcium metal, followed by burning on palladium black, without circulating [3].

After this treatment the oxygen plus helium is compressed by the Toepler pump N into the left hand unit of the fractionating column O (see Fig. 4). The

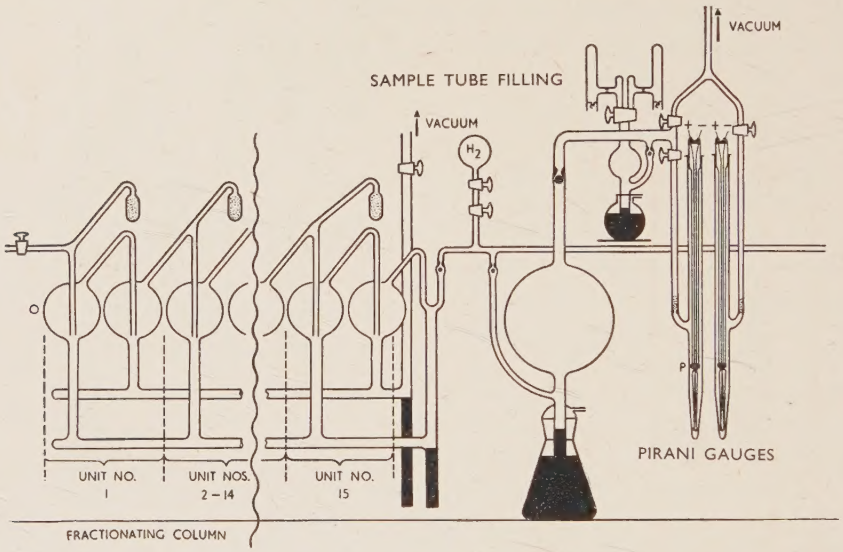

Fig. 4.

helium and, if present, neon, is fractionated off and measured in turn with the Pirani gauge P. The presence of an appreciable amount of neon is an indication of a leak at some stage of the experiment, or of incomplete pumping initially. The relatively few experiments in which this occurred have been discarded as untrustworthy, except in the case of one meteorite (Muonionalusta I). In this isolated case the helium value was so small that about 5 or 7 g of material had to be used instead of the usual 0·1 or 0·2 g, and even then the amount of helium found was only about 10^{-8} cc N.T.P.; so it was hardly surprising that we did not find it possible to exclude neon from air to a considerably lower limit than this. Even so the correction for the contamination by atmospheric helium amounts to only 10 or 15%, so that there can be no error in the figure quoted in Table II, as this is given to one significant figure only.

The operation of the fractionating column has already been reported fully by Glückauf [4]. The method of calibrating the Pirani gauges for helium and for neon using the part of the apparatus shown in Fig. 5 is as follows. A small amount of the gas is let into the McLeod bulb F from the appropriate storage pipette shown. The mercury is then raised to compress the gas into the closed limb, the side tube is pumped out through tap E, and the volume of gas read as usual. The tap E

is then closed, the mercury lowered just to a mark G, with the mercury in the U-tubes A_1 and A_2 raised just to the etch-marks shown. This allows the gas to expand into the carefully calibrated volume of the bulb F and side tubing. By then raising the mercury in C_2 to just above the open end of the inverted U-tube B_2 whose volume has also been carefully calibrated, a known fraction of the original amount of gas is taken. By lowering the mercury in A_2 to a definite mark, the

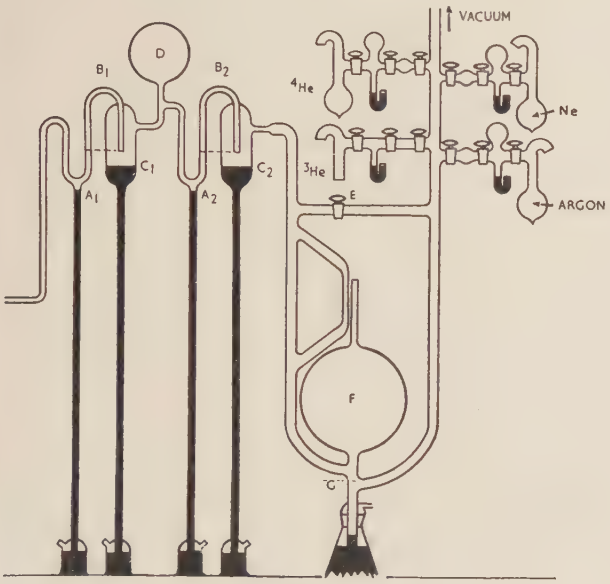

Fig. 5.

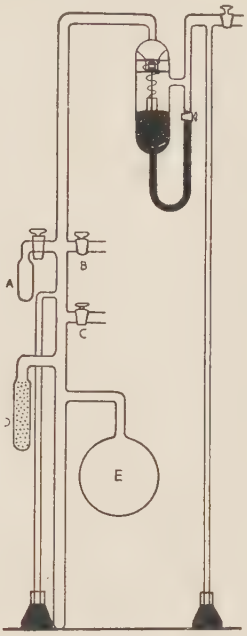

Fig. 6.

fraction of gas is expanded into the bulb D and side tubing, whose volume is also known. This initial fraction is again subdivided by repeating the process with the second pipette B_1, and by lowering the mercury in the U-tube A_1, the final amount of gas is introduced into the Pirani gauge by the same path as the unknown amount of meteoric helium. The pipetting system will deliver an accurately known amount of gas in the range 3×10^{-8} cc to 1×10^{-3} cc.

A word may be said in this section on the method of obtaining pure oxygen. Actually two methods are in current use in our laboratories; either by catalytic decomposition of hydrogen peroxide by means of platinum black, the oxygen then being roughly dried by concentrated sulphuric acid, or by taking ordinary cylinder oxygen via C, Fig. 6, and liquefying it in the tube A. In either case purification is necessary, as contamination with ordinary air is difficult to avoid completely. This is achieved by (*a*) adsorption on charcoal D and pumping off for half an hour or more, and (*b*) liquefaction (in liquid nitrogen) in A and pumping on the liquid by opening tap B to the pumps for one or two seconds several times. The method (*a*) is not very effective in removing neon if present; (*b*) is quite effective but is wasteful of oxygen. Method (*b*) is suitable for a preliminary purification and (*a*) is used to re-purify oxygen, initially pure, which has been stored in the reservoir E for some time and may have become contaminated with helium released from the walls of the glass. This latter effect is quite small as the apparatus is built, except for a part of the Pirani gauges, and the pumps, in soft soda glass, not *Pyrex*, but of course might be important if a meteorite with very low helium content is to be analysed.

Accuracy of experimental technique

1×10^{-7} cc of helium can be handled with ease in our helium apparatus, and measured with an accuracy of 1%. Normally, about 10^{-6} cc of helium were obtained from a sample, and it was found possible to cut down the contamination due to atmospheric helium to better than 1×10^{-8} cc (even this could have been improved, but would have required an inordinately long time for preliminary de-gassing of the vessel walls and reagent during each experiment before commencing dissolution). In all our experiments we have examined the gas obtained for neon; it seems that the natural neon content of meteorites is at least two orders of magnitude smaller than the helium content. Thus the presence of measurable quantities of neon in any analysis has been taken as evidence of contamination by atmospheric gases (including helium) due to some experimental fault. In all cases but one (Muonionalusta I, referred to previously), any such experimental result has been rejected as unsatisfactory.

We intend, however, in the cases where we believe that a large fraction of the helium is due to cosmic ray irradiation, to examine the neon content more closely, since one might also expect the production of neon by this means. This can be done by dissolving much larger samples of meteorite, which, while giving amounts of helium several hundred times larger than those normally needed, will bring the neon amounts, if any, well within the range where they can be handled.

Results

Except where indicated by a limit sign (thus e.g. the helium content of Muonionalusta I is given as $< 0{\cdot}002 \times 10^{-6}$ cc/g) all the values in the tables are believed to be accurate to the extent implied by the number of significant figures, although a small correction should be made now it is known that some meteoric helium contains a proportion of He^3, whereas our gauges were calibrated with pure ^4He. The error involved in neglecting this is at worst a few percent; individual analyses on the same sample were usually concordant to about 1%.

Table 1

Name	*He content* $\times 10^{-6}$ *cc/g*
Muonionalusta I	$<0{\cdot}002$
Muonionalusta II	0·013
Coahuila	0·08
Bethany (British Museum)	0·14
Toluca (Hamburg)	0·16
Uwet	0·21
Braunau	0·43
Staunton	0·85
Serrania de Varas	14·00
North Chilean hexahedrites	
Negrillos	0·56
Filomena	1·18
Puripica	1·29
Rio Loa	1·51
Sierra Gorda	1·68
Coya Norte	2·00

This being so, we may summarise the results in the following way:

Table 1. Isolated cases where the figures by themselves add only to our general knowledge of the range of helium values encountered. For example, Muonionalusta, Coahuila, Serrania de Varas, etc.

The North Chilean Hexahedrite Group. Here it is not certain that all the six samples were originally part of the same

Table 2

Name		*depth (cm)*	*He content* $\times 10^{-6}$ *cc/g*		
Sacramento	A	1	11·20		
Mountains	B	7	11·13		
(See Fig. 8)	C	1	10·9		
	D	8	10·87		
	E	1	10·96		
	F	6	11·62		
	G	1	11·91		
(The distance between A and G is 60 cm)					
Toluca	A	(Distance A to C is 17 cm)			20·7
(Durham)	B	(Distance B to C is 15 cm)		19·32	19·67
(See Fig. 9)	C			19·63	19·82
Toluca	A	(Distance A to C is 18 cm)		19·16	
(Brit. Mus.)	B	(Distance B to C is 14 cm)		19·18	
(See Fig. 10)	C			20·24	
Carbo		0		23·03	
(See Fig. 7)		6		19·05	
		13		17·60	
		21		17·04	
		37		17·06	
Treysa		1	26·07	26·03	
		2	26·43	26·27	
		3	26·91	26·47	
		4	25·13	26·32	
		5	25·55	24·77	26·18
		6	26·42	26·42	
		7	26·86	26·86	
Thunda	A	(Distance from edge 8 cm)		30·27	
(See Fig. 11)	B	(Distance from edge 1 cm)		30·82	

parent meteorite but in view of their chemical and structural similarities and geographical relationship this appears very likely. Without a knowledge of their uranium and thorium content it is impossible to tell whether the range in helium values is due to differences in these; but it may well be that in fact these are the same in all six and the different helium figures reflect the addition to some of them of helium of non-radiogenic origin.

Table 2. In this group samples were taken from different parts of one and the same meteorite to find if there was any variation of the helium content with depth. In Sacramento Mountains, Toluca, and Thunda, there are slight variations which may or may not be caused by inhomogeneities in the uranium and thorium content. In Treysa, there is no detectable variation as we pass from the edge to the centre of this small and roughly spherical [5] meteorite.

Only in Carbo, the most recently investigated object, is a depth effect clearly visible (Table 2 and Fig. 7). The results given for this meteorite are only taken from one

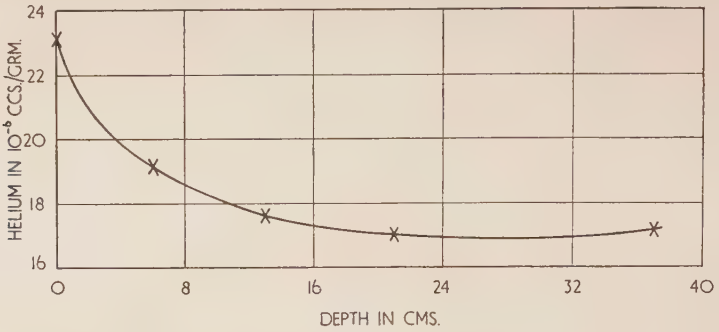

Fig. 7. Carbo meteorite

bore-hole, and further work will be done on samples from other bore holes in an effort to orientate the recovered mass within the pre-atmospheric mass. In addition, work is under way to obtain more information on the effect of cosmic

Table 3

Name of Meteorite	*Helium content in* 10^{-6} *cc/g*	$^3He/^4He$ *in* %
Mount Ayliff	36·8	31·5
Carbo	22·0	28·6
Toluca (Durham)	18·9	29·7
Bethany Amalia (Krantz)	3·4	27·8
Bethany (Harvard)	0·36	17·8

radiation by determining the $^3He/^4He$ ratios at different depths. Table 3 has been published before [6]. A discussion of the possible significance of the $^3He/^4He$ ratios, combined with the depth effect mentioned above, is contained in Part IV.

General Description of the Meteorites Mentioned in Table 2

1. *Sacramento Mountains* (see Fig. 8)

The dimensions of the original mass found were approximately 80 by 60 by 20 cm (see O. C. Farrington, Nat. Acad. of Sciences, Memoirs, Vol. XIII, Washington 1915, p. 391). It was apparently cut into slices in the direction of the 60 cm dimension. The shape of the slices in the possession of the British Museum from which we received our sample can be seen from Fig. 8 on which are visible also the bore holes made for the collection of samples. As Table 2 shows, hardly any variation in the helium content was found although it seems that the left bottom side had a slightly lower helium content than other parts.

2. *Toluca (Durham) and Toluca (British Museum)* (see Figs. 9 and 10)

The meteorite "Toluca (Durham)" consists of a slice of 13·9 kg cut near the crust of an obviously much larger mass. It was bought in Washington as a "nameless" meteorite; its identification as Toluca was possible by comparison with a slice of "Toluca" in the British Museum collections (No. 47192) which clearly comes from the interior of the same meteoritic mass; the two slices show evidence of having been cut on the same lathe, with the Widmanstätten structure in

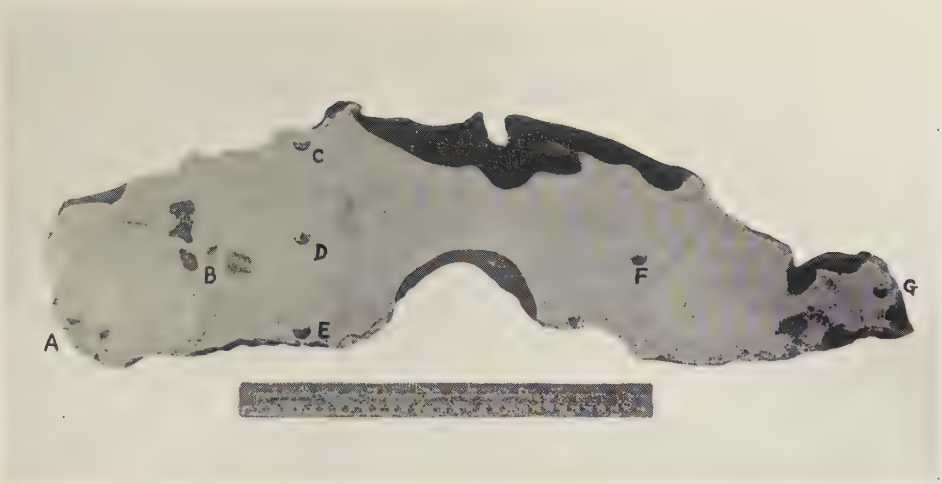

Fig. 8. Sacramento Mountains

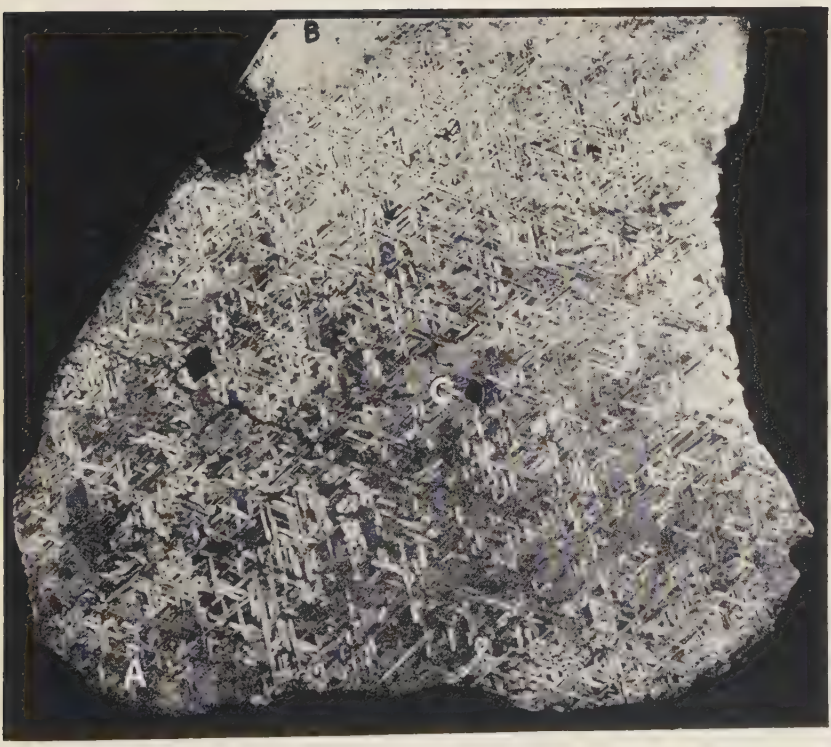

Fig. 9. Toluca (Durham)

Fig. 10. Toluca (British Museum)

Fig. 11. Thunda

identical orientation. They were certainly not adjacent, but it is impossible to say anything definite about their distance apart in the original mass. The closeness of the helium figures found in different places of the two slices shows the absence of a depth effect.

Three samples were taken from Toluca (Durham), one from the centre and two from the edges. Of Toluca (British Museum), one sample was taken from the centre and two from the edges, one of them inside and the other outside. The figures given in Table 2 show no clear variation at all.

Table 4. Survey of the helium content of 68 samples of iron meteorites.

Name of Meteorite	*Class*	*Helium* (10^{-6} cc/g)	*Name of Meteorite*	*Class*	*Helium* (10^{-6} cc/g)
Cape York, Savik	Om	$< 0{\cdot}0002$	Henbury	Om	5
Cape York, Ahnighito	Om	$< 0{\cdot}001$	Cranbourne	Og	5
Muonionalusta I	Of	$< 0{\cdot}002$	Augustinovka	Of	5
Muonionalusta II		0·013	Toluca	Om	6
Coahuila	H	0·08	Arispe	Ogg	7
Bethany (Brit. Mus.)	Of	0·14	Mooranoppin	Ogg	7·5
Bethany, Goamus	Of	0·15	Narraburra Creek	Off	11
Toluca (Hamburg)	Om	0·16	Wichita County	Og	11·5
Bethany Amalia (Foote)	Of	0·2	Sacramento Mountains	Om	11·2
Bethany Gröndorn	Of	0·2	San Angelo	Om	12
Bethany, Lion River	Of	0·2	Serrania de Varas	Of	14·0
Uwet	H	0·21	N'Goureyma	Ob	14
Bethany (Harvard)	Of	0·36	Cosby's Creek	Og	14
Braunau	H	0·43	Hraschina	Om	15
Negrillos	H	0·56	Seneca Falls	Om	15
Staunton	Om	0·85	Charcas	Om	16
Canon Diablo	Og	1	Silver Crown	Og	17
Cape York, Dog	Om	1	Staunton County, Mass III	Om	19
Cape York, Woman	Om	1	Staunton County, Mass V	Om	19
Magura	Og	1	Joe Wright Mountain	Om	19
Filomena	H	1·18	Burlington	Om	19
Puripica	H	1·29	Toluca (London and Durham)	Om	20
Rio Loa	H	1·51	Nelson County	Ogg	20
Sierra Gorda	H	1·68	Williamstown	Om	21
San Martin	H	1·70	Lenarto	Om	22
Coya Norte	H	2·00	Carbo	Om	22
Sao Juliao de Moreira	Ogg	2	Carthage	Om	25
Seeläsgen	Ogg	2	Treysa		26·5
Murnpeowie	Og	2	Yardea	Om	30
Mount Joy	Hb	2	Thunda	Om	30·5
Copiapo	Ob	2·5	Mount Ayliff	Og	37
Bethany, Amalia (Krantz)	Of	3·44	Morden		40
Santa Rosa	Ob	3			
Nejed	Om	4			
Tamarugal	Om	4			

3. *Carbo* (see Fig. 7)

The shape of the meteorite is further away from a sphere than Treysa. The hole was drilled to the depth of 40 cm to what is more or less the centre of the mass in its present shape. It was found that there was a very clear decrease of helium content with depth as can be seen from

the table and the graph (Fig. 7). That at the end of the hole there seems to be a slight increase may be due to the fact that the centre of the original mass has already been passed by the drill hole.

4. *Treysa*

As mentioned before this meteorite is fairly spherical. The samples (drillings) were taken along a radius at one centimetre intervals. No significant variation was found.

5. *Thunda* (see Fig. 11)

The very irregular shape of this piece in the possession of the British Museum is shown in Fig. 11. Some samples were taken near the crust, others as much to the centre of the piece as possible. The helium content near the crust is slightly higher than in the centre.

Appendix. The Beddgelert Meteorite

In addition to iron meteorites we have studied the helium—and also the uranium and thorium—content of one stone meteorite. A full description of the phenomena of fall and the chemical and radiochemical composition of this meteorite have already been given elsewhere [7], but a few more details are given here for the sake of completeness.

The Beddgelert meteorite was analysed within a year of fall for helium, uranium and thorium (in the case of helium within a few weeks). The following table gives the results of these analyses for the iron and stone phase separately.

	He $\times 10^{-6}$ cc/g	U $\times 10^{-8}$ g/g	Th $\times 10^{-8}$ g/g
Metal phase	2·8	9·1 ± 1	8·5 ± 4·9
Silicate phase	30	10·8 ± 2·7	39 ± 8

In the case of the iron-phase helium it was found that the value obtained was a function of the size of the iron-nickel granules, the coarser ones containing about $2{\cdot}0 \times 10^{-6}$ cc per gram and the finer ones (extending down to the finest dust) about $5{\cdot}0 \times 10^{-6}$ cc per gram. The figure in the table is the weighted mean of the experimental results and is thought to be accurate to about 5%. The ages of the two phases, based on the above figures and the assumption of a purely radioactive origin of the helium, are

Fe phase about 2×10^8 years.

Si phase about $1{\cdot}2 \times 10^9$ years.

It is not easy to be sure about the significance of the difference in the apparent ages of the two phases. From a microscopic examination of the stony phase it is clear that the latter is composed of many different materials, some of them roughly like spherical pebbles (the chondrules) and others of irregular shapes, together with a dark coloured ground mass referred to by Dr. Campbell Smith [7] as glass. The chondrules evidently consist of a fairly wide variety of chemical species and while some appear to contain glassy material others contain smaller

chondrules of different composition; some are completely surrounded by glass and it seems probable that all the iron-nickel fragments are enclosed in a very thin shell of glass. Clearly the present stone is made up of fragments of very different origins, of which some may have solidified at a much earlier date than others. These fragments were compacted together, with the iron-nickel fragments derived from still another source and whose "average age" was apparently far less than that of the stony material. Whether some of this extremely complex mixture was in the molten state when the compaction process took place it is impossible to say; the presence of so much glassy material argues a heating or re-heating at some stage and of course this may well have been simultaneous with the time of formation of the meteorite as a whole. Perhaps also the mass was subjected to high pressure, which may explain its great hardness. But even if the possibility of helium production by cosmic rays is taken into account, one has to face difficulties in explaining why the silicate phase should have more than ten times the amount of helium per gram as the iron phase; some helium may be of cosmic ray origin, but if both the iron and stone phase have been exposed to the same irradiation, their content of cosmic ray helium should be nearly the same, as the generation of helium in iron by cosmic rays is thought to be not much less than in stone. The conclusion therefore seems unavoidable that the bulk of the iron phase solidified later than the bulk of the stone phase.

It is unfortunate that it is not possible with existing techniques to separate the individual chondrules and perform analyses on the different species separately; such experiments might conceivably be performed as far as the helium is concerned, as only about one tenth of a gram is needed, but such helium figures would be of little value themselves without the uranium and thorium, for which quantities of material of the order of 20 grams are essential in order to get reasonable statistical accuracy in the counting.

We wish to thank Professor F. A. Paneth who suggested the work, for his continued interest and for many useful discussions.

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Recent studies on iron meteorites. III

Determination of the uranium and thorium contents

J. C. Dalton, J. Golden, G. R. Martin, E. R. Mercer and S. J. Thomson

Londonderry Laboratory for Radiochemistry, University of Durham

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ABSTRACT

Methods are described for the isolation of uranium and thorium, and some of their radioactive disintegration products, from 10 to 100 g samples of iron meteorites. The concentrations of these elements were of the order of 10^{-8} g per g of meteorite. The methods used were liberation of radon and thoron, and classical co-precipitations and solvent extractions for isolation of uranium, ThB and ThC.

Estimations of uranium by two methods are described, counting of radon in equilibrium with the uranium series in a gas counter, and fluorimetry. Thorium estimations were accomplished either by thoron gas counting or by α-particle scintillation counting of equilibrium amounts of ThC in a counter of extremely low background.

1. Introduction

In connection with the meteorite studies undertaken in this laboratory [1], it has been necessary to determine the uranium and thorium contents of a number of meteoritic irons. The concentrations involved are of the order of 10^{-9} to 10^{-8} g of uranium or thorium per g of meteorite, and we propose in this paper to discuss the techniques which we have utilised to effect such determinations with the limited quantities (10–100 g) of the materials available.

Neither for uranium nor for thorium does there appear to be a suitable straightforward chemical method; even the most sensitive colorimetric methods [2, 3] hardly appear to be applicable to sub-microgram quantities.

The most obvious technique to employ is the estimation of the radioactivity naturally associated with these two elements and their disintegration products. The major difficulty arises from the need to extract from a vast excess of meteoritic material (essentially an iron-nickel alloy) the appropriate radioactive substance in a form suitable for the counting of the particles emitted. We have rejected the counting of β-particles from any of the daughter substances [4] on account of the difficulty of achieving sufficiently low natural background effects with β-counters. The counting of α-particles can, however, be satisfactorily carried out at much lower levels of activity, and we have used first the counting of α-particles from radon and thoron in equilibrium with radium and thorium X contained in the meteorite [5, 11], and, latterly, the counting of solid sources of Th(B + C) by means of a scintillation counter. In this instrument we have achieved a background counting rate of about 1 disintegration per hour by careful exclusion of all "contaminated" materials from the effective part of the apparatus. For thorium this method appears to be the best of those available to us, but for uranium we have increasingly utilised a fluorimetric method [6], which depends upon the measurement of the fluorescence excited by ultra-violet light in a solid solution of uranium in sodium fluoride. This involves the quantitative extraction

of uranium from the meteorite, and its purification from interfering elements, and methods are presented for making the necessary separations in a quantitative manner.

The radioactivation method recently described by A. A. Smales [7] would also appear to be potentially useful for meteorite work, although it would apparently be necessary to effect a preliminary enrichment of the uranium before irradiation, and much of the appeal of the method is thus lost.

In all this work, a major problem is the achievement of satisfactory "blank" measurements; especially is this the case when large quantities of iron meteorite must be dissolved and subjected to chemical treatment. Accordingly, we give in Appendix I an account of the source of our reagents, and the steps taken to ensure the introduction of minimal amounts of contamination during the extraction and working up of the materials to be measured.

2. The Radon-Thoron Method

In an iron meteorite of age greater than about 10^6 years it may be assumed that radioactive equilibrium has been established, and it is therefore sufficient, for uranium or thorium estimations, to determine any one member of the radioactive series involved. A method which has certain desirable features from the chemical point of view involves the separation, using barium as a carrier, of the radium isotopes from both series (^{226}Ra and ^{224}ThX), and estimating these by counting the α-particles from their rare gas daughter products (^{222}Rn and ^{220}Tn). Direct extraction of the radon from a solution of the meteorite without preliminary separation of the radium would be possible, and has been done [8, 11], but such a method is less satisfactory for thorium determination on account of the short half-life (54 sec) of thoron; it is necessary in practice to employ quantities of meteorite of the order of 50 g, and the volume of solution thus involved results in a poor emanating efficiency for the thoron. We thus always carry out a preliminary separation of the radium isotopes, using barium as carrier, in order to reduce the volume of liquid from which the emanation has to be extracted.

Chemical separation

The sample of the meteorite, of the order of 50 g, is dissolved in hydrochloric acid, care being taken to minimise loss in spray. Any residue is removed by centrifugation, and brought into solution by the use of one of the following reagents, as appropriate: (*a*) conc. nitric acid; (*b*) HF + $HClO_4$ aq.; (*c*) I_2–KI reagent [9]; (*d*) fusion mixture. The main (chloride) solution and the solution of the residue are then separately extracted by precipitating radium sulphate from each; 50 mg of barium chloride is normally used as carrier.

The precipitates are allowed to stand overnight on a waterbath, and then centrifuged off, washed, and transferred to a platinum crucible, in which they are fused with an excess of fusion mixture (1–2 g). The cooled melt is leached with water, and the barium carbonate so obtained separated by centrifugation and subjected to a further treatment with fusion mixture to ensure the complete removal of sulphate. The barium carbonate is finally dissolved in a slight excess of dilute hydrochloric acid, and the solution placed in a bubbler for measurement.

Measurement

Radium and thorium X are then estimated by counting, in a nitrogen filled ionisation chamber, the α-particles from the radon and thoron in radioactive equilibrium with them. Because of the short half-life of thoron, it is necessary to carry out the counting of the α-particles from this component of the mixture in a flow system; fortunately, it is not difficult so to arrange the rate of flow that virtually all the observed disintegrations relate to the thorium series, the half-life of radon being long enough to ensure that only a minute proportion of it will disintegrate whilst it is within the ionisation chamber. Furthermore, the relatively short half-life of thorium X, the parent of thoron, makes it necessary to carry out the thoron measurement before the radon measurement.

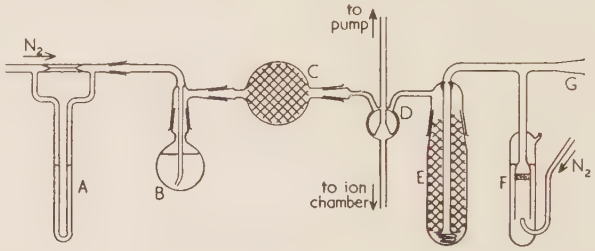

Fig. 1. Apparatus for radon and thoron determination.

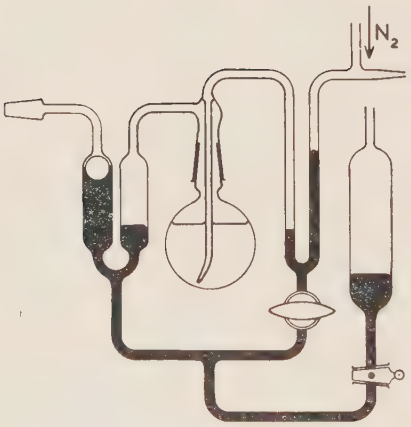

Fig. 2. Radon unit.

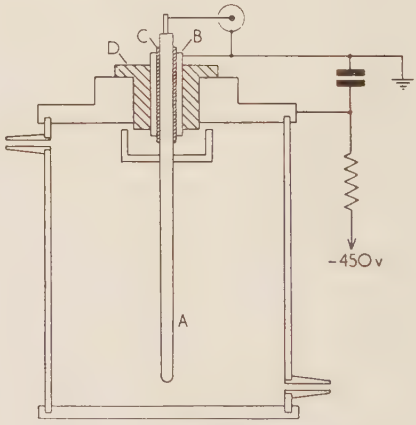

Fig. 3. Ionisation chamber for radon and thoron counting.

The counting of the thoron α-particles is carried out with the apparatus shown in Fig. 1. A stream of nitrogen ("specially pure" nitrogen supplied by the *British Oxygen Co., Ltd.*, stated to contain less than 10 p.p.m. of oxygen) is passed through the flow-meter, *A*, and the bubbler, *B*, which contains the ThX and Ra with their barium carrier, in aqueous solution. The nitrogen stream, carrying the thoron, is then dried over caustic potash pellets in *C*, and admitted through the special three-way tap *D* to the ionisation chamber, shown in detail in Fig. 3.

It is clear that there will be an optimum nitrogen flow rate which will depend upon the volume of the ionisation chamber, and upon the "dead space" between

the bubbler and the chamber. Too slow a rate of flow will result in too much of the thoron having decayed before reaching the chamber, whilst too fast a flow will cause a loss of efficiency through thoron being swept through the chamber before decaying.

Urry [10] has calculated the optimum flow rate as a function of these two parameters, although he does not take account of the average time spent by a newly formed thoron atom in the solution before entering the gas stream. We have found empirically that the optimum flow rate for our set-up (chamber volume 910 cc and dead space 40 cc) was 220 cc/min, and this has been adhered to throughout the work.

Calibration of the thoron counting system was effected by comparison with a solution made by dilution from a solution of chemically pure thorium nitrate standardised gravimetrically. The thorium salt from which this solution was prepared was old enough (about 40 years) to ensure that secular equilibrium between thorium and radiothorium had been re-established. Our apparatus gives $6{\cdot}5 \pm 0{\cdot}4$ disintegrations per hour per microgram of thorium.

The natural background count of the chamber is measured before and after each thorium measurement by substituting a clean empty bubbler for that containing the thorium X solution, and by passing the nitrogen through at the standard flow rate. The mean background counting rate is subtracted from the counting rate observed with the solution. Typically, the background estimated in this way would be about 30 disintegrations per hour. Allowance is, of course, made for decay of the thorium X during the period which elapses between the precipitation of the barium sulphate and the start of the counting.

After completion of the thorium measurement, the bubbler is attached to a "radon unit" [11] (Fig. 2). The air in the apparatus is displaced by pure nitrogen, and the sample sealed off by raising the mercury in the U-tubes at each side. The sample is kept sealed in this way for a period of about 10 days, during which time the radon grows towards secular equilibrium with the radium in the sample.

For counting, the radon unit is attached to the apparatus at *G* (Fig. 1), and the ionisation chamber and connecting tubes evacuated. Pure nitrogen is then admitted through the sintered glass-mercury seal *F* until the pressure in the connecting tube is equal to that in the bubbler; the mercury in the U-tubes is then lowered, *D* opened carefully, and nitrogen allowed to pass through the bubbler carrying the accumulated radon into the ionisation chamber. Water vapour is removed by passage through the trap *E*, packed with caustic potash pellets. When the chamber has been filled to atmospheric pressure, the mercury cut-offs can again be raised, and counting started. As for the thorium measurements, counts are taken of the natural background effect before and after each run, and the mean background counting rate subtracted from that observed during the run.

Calibration of the apparatus was effected by means of a radium chloride solution originally prepared by R. B. Jacobi [8], and standardised at the Vienna Radium Institute. Our apparatus gives 194 ± 4 counts per hour per 10^{-12} g radium at equilibrium. The uranium content of a sample can then be calculated, making the assumption that the radium is in secular equilibrium with the uranium, and allowing for any lack of equilibrium between the radium and radon.

Details of counting equipment

The ionisation chamber used is that previously employed by Arrol, Jacobi and Paneth [11], subject to some modification. The brass collecting electrode, A, is insulated from the earthed guard ring, B, by a silica tube, C. The guard ring is in turn separated from the body of the chamber by a polystyrene insulator D. The chamber itself is of steel, nickel plated to reduce the natural alpha activity of the metal, and the whole instrument is made vacuum tight by means of wax, carefully applied to avoid fouling the insulating surfaces. The insulators are screened from the active volume of the chamber by means of an "umbrella" attached to the collecting electrode. The chamber is connected by means of thick-walled rubber tubing to the remainder of the system, in order to reduce the transmission of mechanical vibration from the latter; electromagnetic interference is eliminated by housing the whole chamber assembly in an earthed copper screening box.

Negative-going pulses, representing the collection of electrons at the central electrode of the ionisation chamber, are fed through a short length of polythene-insulated cable to the first stage of a resistance-capacity-coupled linear pulse amplifier, modified from the "type 1002" amplifier [12] built for the Atomic Energy Research Establishment, Harwell. The output from this amplifier is displayed on a cathode ray oscilloscope for visual checking, and fed also to a pulse amplitude discriminator based on a design by Cooke-Yarborough [13]. By suitable choice of the level of discrimination it can be arranged that pulses due to α-particle ionisation in the chamber are passed to the recording mechanism, whereas the random amplifier noise is effectively rejected. Since the average rate of arrival of pulses is rarely more than 1 or 2 per minute, no electronic scaling circuit is normally used and the discriminator output is used directly to trigger a "flip-flop" circuit driving a mechanical counting meter. A simple pen recorder, connected in parallel with the mechanical meter, provides a useful check on the reliability of the recorded results.

The rather long resolving time (about one-eighth of a second) of the mechanical meter has the advantage of making the whole system relatively insensitive to microphonic interference, since it will, in general, respond only once to a damped train of impulses which would very often register a number of times on an instrument with a shorter resolving time.

Statistical error

By virtue of the low uranium and thorium contents of the materials investigated, and the limited quantities generally available, the random "sampling errors" inherent in the counting procedure are comparatively large. Due allowance is made for the fact that the α-particle counts recorded are not all independent events, since in each series two members of the active deposit may contribute in addition to the rare gas members. With each result we have quoted standard deviations calculated on the basis of the sampling errors in the counting measurements.

Results

These are shown in Table 1.

3. Fluorimetric Estimation of Uranium

It has been known for some time that extremely dilute solid solutions of uranium in sodium fluoride give a strong yellow-green fluorescence when irradiated with ultra-violet light; this phenomenon has been utilised, for example, by Hernegger and Karlik [6] for the estimation of uranium in sea-water. More recently, a direct-reading objective fluorimeter suitable for such work has been developed at the Atomic Energy Research Establishment, Harwell, and the instrument we have used is a slightly modified version of the A.E.R.E. fluorimeter type 1080A [14]. The ultra-violet source in this instrument is a 125W commercial high pressure mercury arc from which the glass envelope has been removed; the light is filtered through a 4 mm thickness of Chance's OX1 glass, and focused by means of a quartz lens on to the layer of fused sodium fluoride. Fluorescent light, filtered through 4 mm thicknesses of Chance's OB2 and OY13 glasses, is focused on to the cathode of a 931A multiplier photocell, the output of which is amplified and measured. To reduce the amplification of the thermal noise from the multiplier tube, the amplifier is tuned fairly sharply to 100 cycles, the frequency at which the fluorescent light is interrupted (it will have twice the periodicity of the 50 cycle mains from which the U.V. lamp runs). The whole equipment was operated from an electromechanically stabilised mains supply, and no trouble was experienced from mains voltage fluctuations.

Preparation of sodium fluoride beads for fluorimetry

Uranium solutions for analysis are evaporated under radiant heaters on platinum trays of diameter 20 mm and capacity 1·5 to 2 ml. The trays are placed on a platinum wire triangle, 0·94 g of sodium fluoride are added, and they are then heated with a Méker Burner using coal gas and compressed air. Heating is continued for 25 seconds after the last crystal of sodium fluoride melts and after cooling the beads for five minutes they are examined in the fluorimeter.

Heating the fluoride for times less than 25 seconds produces inhomogeneous beads and prolonged heating causes volatilisation of sodium fluoride and attack by the fluoride on the platinum metal with consequent quenching of fluorescence (c.f. [15]).

Of the elements which produce interference in fluorimetric determinations, iron and aluminium will be considered first. The fluorescence of a sodium fluoride bead containing one microgram of uranium with added iron and aluminium, is shown in the following table. It may be noted that the tolerance found for aluminium is considerably higher than that found by Jacobs[15].

Wt. of Fe or Al in microgram in each bead	0	1	2	5	10	20	50	100	200	500
Scale readings in arbitrary units. Fe	1200	1200	1190	1080	1030	1010	890	860	380	250
Scale readings in arbitrary units. Al	1200	1200	1200	1200	1180	1170	1210	1190	1160	1120

By the addition of 1 microgram amounts of uranium to the beads produced in the meteorite estimations and observation of the fluorescence after drying and re-fusing the beads, it was shown that quenching by aluminium and iron was negligible. Calculations also indicated that under the experimental conditions described, the amounts of iron and aluminium passing into the sodium fluoride were negligible. Relevant partition data were obtained from Irving's survey [16]. Two elements which are reported [18] to interfere with fluorescence measurements of uranium by enhancing the fluorescence are niobium and tantalum. These elements are present in iron meteorites to the extent of 0·20 and 0·06 g per ton [17] (cf. uranium 0·001 g/ton) and although no data are available on their extraction by the procedures to be described, it would seem most improbable that these elements will interfere in the present estimations. Experiments showed that 10^{-8} to 3×10^{-3} g of niobium and 10^{-6} to 10^{-5} g of tantalum, per sodium fluoride bead, did not cause fluorescence; quenching or enhancement of uranium fluorescence were not observed. It has been reported [18] that 500 μg of niobium give the same fluorescence as 0·3 μg of uranium and 50 μg of tantalum the same as 0·6 μg of uranium. Rodden [3] has suggested that these results may be due to uranium in the niobium and tantalum samples used.

Contributions to the fluorimetric measurements made by uranium in the reagents are measured by carrying out the procedure with the reagents alone.

Nine beads are usually prepared in each meteorite estimation and in each experiment on the reagents alone. Combination of the results allows an estimate to be made of the probable error for each estimation.

Calibration of the apparatus is effected on each occasion by means of sources made up from aliquots of a solution prepared from "AnalaR" uranyl nitrate hexahydrate standardised gravimetrically.

4. α-Particle Counting with Scintillation Counter

An important development in particle counting techniques during the last few years has been the application of the electron multiplier phototube to the counting of the scintillations produced in suitable phosphors. From the point of view of the present work the great advantage of this method lies in the very low natural background counting rates which can be achieved, provided that certain simple precautions are observed. In the apparatus we have used, background effects associated with thermionic emission from the phototube appear to be entirely negligible, and the residual background counting rate of about 0·9 c per hour appears to be due to natural α-particle contamination of the phosphor; it is, in any event, no longer a serious obstacle. To achieve this low rate we have eliminated all glass and metal components from the α-particle-sensitive region, an organic polymer material (*Perspex*) being used exclusively for source mounts, phosphor mount, and constructional material. A most important precaution is the minimisation of the volume of air to which the phosphor is exposed, especially when the high voltage is applied to the photocathode; radium active deposit collected from the radon naturally present in air can materially increase the background counting rate if this consideration is overlooked.

The construction of our scintillation counter is shown in Fig. 4; it is housed

in a light-tight metal box, the door providing access to the source compartment being interlocked with the high voltage supply, to prevent the phototube being energised whilst the door is open. After exposure to light, the phosphor (silver-activated, "nickel-killed" zinc sulphide, type G86, kindly supplied by the Levy West Laboratories, Wembley) shows some slight phosphorescence, but this decays within a few minutes, and does not, in any case, add materially to the background counting rate.

Pulses from the final anode of the multiplier tube (11-stage E.M.I. type 5359) are further amplified by a three-stage resistance-capacity-coupled amplifier with negative feed-back, and passed to a pulse amplitude discriminator. Pulses above the predetermined discriminator level are recorded on an electromechanical counter, and, simultaneously, on a drum recorder. For counting more active sources, the electro-mechanical counter can be replaced by an electronic scale-of-100 counter.

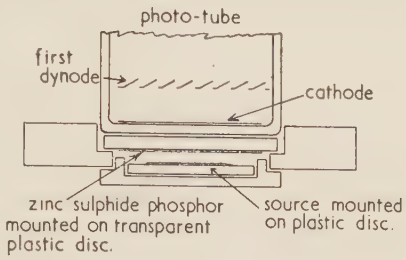

Fig. 4. Arrangement for low-background scintillation counting of solid sources.

This method can, in principle, be applied to the determination of any of the α-active members of either the uranium or thorium series, but certain practical limitations must be considered. We have rejected the counting of radium or thorium X on account of the difficulty of preparing non-emanating sources; polonium has also been rejected on similar grounds. Thorium and ionium are both so long-lived as to preclude the counting of thorium isotopes from materials containing both thorium and uranium. Uranium itself could well be counted, but having extracted it in a form suitable for counting, the fluorimetric technique can equally well be applied, and gives a rather higher sensitivity and accuracy. We have not, in fact, used this method for the uranium-radium series, but have confined it to the determination of ThC in equilibrium with ThB, extracted after growing to equilibrium with the radiothorium content of the sample.

Th(B + C) is readily separated by precipitation as sulphide with a small quantity of lead as carrier, and the half-life of ThB (10·6 hours) is short enough to permit several successive extractions to be made, thus increasing the statistical accuracy of the determination. An initial scavenging operation is necessary to remove the corresponding isotopes belonging to the radium series, but thereafter no interference from this source is to be expected, provided Ra has been effectively removed. The lead sulphide precipitate, carrying the Th(B + C), is separated by centrifugation, dissolved in conc. HCl, and evaporated on to a *Perspex* disc, and dried by radiant heat with a current of air playing radially on the disc [19]. A standardised counting routine is adopted (16 hours counting, starting 1 hour after precipitation). The apparatus has been calibrated by means of an "old" thorium solution previously standardised gravimetrically.

5. Chemical Separation of Uranium and Thorium

Isolation of uranium by solvent extraction

The following technique is applied when only 10 to 15 g of the meteorite are available. In this case only the uranium can be determined, the amount of

thorium present being too small for analysis. The average composition of the starting material is 90% iron, 9% nickel with small amounts of other elements, including cobalt, chromium, and copper.

10–15 g of the meteorite are dissolved in dilute nitric acid: concentrated nitric acid and 50 g ammonium nitrate are added to the solution and its volume then reduced by evaporation to about 75 to 100 ml. The uranium can be extracted from this solution by shaking it four times with 75 ml portions of ether [20]. The nitric acid concentration is maintained at a suitable level by the addition of 10–20 ml concentrated acid after each extraction [21]. The reducing effect of the ether is counteracted by boiling the nitric acid solution after each extraction and the uranium thereby maintained in the hexavalent state. By this process the uranium is quantitatively removed into the ether layers: direct estimation of the uranium is not however possible at this stage, for about 1% of the total iron accompanies the uranium [16] and this is removed with negligible loss of uranium as follows.

The combined ether layers are shaken twice with 50 ml portions of concentrated nitric acid which has been saturated with ammonium nitrate. The iron and some of the uranium are thus removed from the ether solution. The uranium is recovered from the nitric acid solution by two extractions with 50 ml quantities of ether, which are combined with the main ether extract.

It was found that the ether layers at this stage retained small droplets of the aqueous phases and these droplets contained sufficient iron to interfere with the estimation of the uranium, by imparting a colour to the sodium fluoride beads prepared for fluorimetric estimation of the uranium. These traces of iron are therefore removed by the following procedure. The ether extracts are evaporated with 300 ml water containing 25 ml concentrated ammonium hydroxide (forming ammonium nitrate *in situ*) and the aqueous solution remaining is cautiously reduced to 75 ml; 10 ml concentrated nitric acid are added and the uranium extracted as before with four portions of ether: by this process the amounts of iron are reduced to below the interference limits. These final ether extracts are evaporated with 250 ml water and the aqueous portions concentrated, made up to 10 ml, and 1 ml portions taken for the uranium estimations. These are evaporated to dryness by radiant heat in small platinum trays, fixed amounts of sodium fluoride added and the mixture fused under standard conditions. The fluorescence of the solid solutions produced is measured in a fluorimeter.

By the method described, 10 to 15 g samples of iron meteorites were analysed for uranium content with an accuracy of the order of 10%. The overall reagent blanks for uranium are about 10 to 20% of the amounts of uranium in the meteorite samples. Results obtained are shown in Table 1.

The development of the method had been made initially by preparing solutions of meteorite-like composition, viz. solutions of steel in nitric acid. Any uranium originally present was extracted by ether using the procedure described and the uranium-free solution was then divided into two parts. One was used for a reagent blank. To the other was added a known amount of isotopically pure ^{233}U. Complete recovery of the uranium by the procedure described was shown by α-particle counting of the ^{233}U in a parallel plate ionisation chamber for solid sources. An apparent recovery of $104{\cdot}5 \pm 2{\cdot}8\%$ was achieved.

Estimation of uranium and thorium in a meteorite sample

Minimum quantities of about 40 g of a typical meteorite are needed to give sufficient thorium activity for counting, and when such quantities are available the following technique, which permits the determination of uranium and thorium on one sample, is employed.

The method involves removal of iron from the meteorite solution by solvent extraction, followed by co-precipitation of uranium and thorium under standardised conditions with added iron and aluminium. The uranium and thorium are then separated by a hydrogen peroxide-sodium hydroxide treatment using aluminium and iron as their respective carriers. Measurements of uranium contents are made by fluorimetry and of thorium by α-particle scintillation counting.

About 40 g of meteorite are dissolved in concentrated hydrochloric acid and any residue which remains is dissolved in either nitric acid or a mixture of hydrochloric and nitric acids. Before ether extraction of the iron any ferrous iron present is oxidised either by chlorine gas, by warming with potassium chlorate, or by boiling with concentrated nitric acid. The solution is evaporated to dryness on a waterbath and the residue dissolved in 6·5N hydrochloric acid. The iron is then extracted from the solution by shaking it with 250 ml portions of ether [16] (previously equilibrated with 6·5N hydrochloric acid) until thiocyanate tests indicate almost complete removal of iron from the aqueous layer. (Experiments showed that about 0·1% of the uranium is lost at this stage.) It is reduced to half its volume by evaporation and then an equal volume of distilled water is added: the hydrochloric acid is then at a convenient concentration, viz. about 2N. At this stage traces of silica are sometimes precipitated and estimations made using added uranium and UX1 showed that about 0·1% of the uranium and 0·5 to 0·1% of the thorium are then lost.

To this solution 20 mg of aluminium (as aluminium chloride), 10 mg of iron (as ferric chloride) and 10 mg barium (as chloride) are added. Ammonia gas, prepared from sodium hydroxide and ammonium hydroxide, is used to precipitate iron and aluminium as (carbonate free) hydroxides, thus co-precipitating the uranium and thorium. The barium acts as a "hold back" carrier for any radium in solution and any copper present remains in solution as a cuprammonium complex. The decay products of the former element would interfere in subsequent α-particle counting, the latter in the precipitation of the ThB. As a precautionary measure against adsorption of radium or copper, the hydroxide precipitate is centrifuged, collected, dissolved in dilute hydrochloric acid, 10 mg of barium added, and the hydroxide re-precipitated.

The precipitate, after being centrifuged and collected, is dissolved in 5–10 ml dilute nitric acid and 10 mg barium added. The solution is then ready for the separation of the uranium and thorium: it is poured into a mixture of 30 ml 20% by weight sodium hydroxide and 30 ml 20 volume hydrogen peroxide, immediately warmed to the boiling point and rapidly centrifuged. (Delay at this stage brought about loss of uranium, probably by decomposition of the peroxyuranate with consequent deposition of uranium on the precipitated iron hydroxide.) The thorium precipitates with the iron hydroxide and the uranium remains in solution with the aluminium. The suspension is centrifuged and the uranium is recovered

from the liquid phase by boiling the liquid with concentrated nitric acid and by extraction of the uranyl nitrate so formed with ether, after addition of ammonium nitrate as salting out agent: trials showed that the extraction efficiency is 99·7%. The extraction of the aluminium present at this stage in the aqueous layer is inhibited by the presence of the sodium nitrate [20]. The adverse effects which the aluminium has [15] on the preparation of sodium fluoride beads for fluorimetry have been discussed earlier.

Thorium recovery and estimation in the combined uranium-thorium method

The iron hydroxide precipitated from the peroxide treatment with its accompanying thorium and radiothorium is centrifuged off and the supernatant liquid removed. The precipitate is dissolved in hydrochloric acid and the solution diluted to 25 ml: the quantity of acid used is such that the acid strength is 0·2N. 10 mg of barium, as chloride, are added as "hold back carrier" for the radium isotopes and the solution is then stored for 1 month during which time the ThX ($t_{\frac{1}{2}}$ 3·64 d.) grows to equilibrium. 2 mg lead, as acetate, are added to the solution and precipitated with hydrogen sulphide. The precipitate produced is discarded because of possible contamination with members of the uranium-radium disintegration series. After 3–4 days ThB and C have grown to equilibrium from the ThX in solution. Further addition of 2 mg of lead and precipitation gives precipitates containing ThB and C in equilibrium amounts.

The suspensions of lead sulphide with the ThB and C are centrifuged and the precipitates dissolved and counted as described earlier. Repeated extractions of ThB and ThC from a meteorite solution showed that none of the parent elements suffers any loss in this procedure. Tracer experiments showed that the fifth and sixth precipitations gave $100 \pm 3\%$ of the expected number of counts. Decay curves indicated however that loss of the parent elements from the solution occurred if the centrifuging process was continued beyond five minutes.

The amounts of thorium in the original meteorite are computed from comparison of the counts obtained with those from lead sulphide sources prepared under identical conditions from the standard thorium solution described in the paragraph dealing with the radon-thoron method.

An advantage of this method is that a number of active lead sulphide deposits can be prepared from the one meteorite solution. In several cases spurious counts were observed in the first one or two lead precipitations, later precipitations producing sources of constant activity. That this activity was probably due to polonium was shown as follows. Samples of lead sulphide precipitates were prepared from the silicate phase of a meteorite in which the uranium series would be present in quantity and in equilibrium, and an estimate made of the half life of the long lived isotope accompanying the first lead sulphide precipitate. The half life of the species was of the order of 130 days, indicating that the element present was probably polonium. The overall reagent blanks for uranium and thorium in this procedure are about 20% and 50% respectively of the amounts in the meteorite samples.

Results

These are shown in Table 1.

Table 1.

Meteorite	*Uranium in* 10^{-8} g/g			*Thorium in* 10^{-8} g/g	
	Radon method	*Fluorimetric direct extraction method*	*Fluorimetric combined* U-Th *method*	*Thoron method*	*Scintillation counting combined* U-Th *method*
Ahnighito	0·21 ± 0·08	0·56 ± 0·05		0·77 ± 0·45	
Bethany (Amalia Krantz)			0·53 ± 0·05		0·92 ± 0·63
Bethany (Harvard)		1·14 ± 0·03	0·61 ± 0·03		2·46 ± 0·58
Brenham Township (Iron Phase)		0·06 ± 0·02	0·05 ± 0·02		
Carbo		0·45 ± 0·03 0·56 ± 0·04	0·52 ± 0·02		0·63 ± 0·42
Carthage		0·41 ± 0·05			
Coahuila	⩽ 0·5			⩽ 0·93 ⩽ 1·02	
Muonionalusta I	0·88 ± 0·13			1·10 ± 0·88 1·83 ± 0·96	
Muonionalusta II			0·20 ± 0·04 0·18 ± 0·01		⩽ 1·1
San Martin		0·77 ± 0·03	0·75 ± 0·04		10·4 ± 1·4
Savik	0·20 ± 0·05 0·22 ± 0·05	0·21 ± 0·03	0·18 ± 0·02	⩽ 0·24 ⩽ 0·26, ⩽ 0·21	
Thunda		0·55 ± 0·04			
Tocopilla	2·30 ± 0·30		0·72 ± 0·03	1·90 ± 0·80	⩽ 1·00
Toluca Durham	0·86 ± 0·30		0·65 ± 0·05 0·52 ± 0·06	⩽ 1·05	⩽ 0·60
Treysa	0·70 ± 0·30			5·90 ± 2·40 5·10 ± 1·20	

Notes: (1) Errors quoted for results obtained by an α-particle counting technique are standard deviations based on the random errors inherent in the numbers of disintegrations recorded in the relevant measurements; for analyses by the fluorimetric technique, the standard deviations refer to the internal consistency of the sets of nine measurements made on aliquots of the solution finally obtained.

The radon and thoron methods are not only, in general, less reliable in this respect, but are also more liable to be in error through contamination; we are thus inclined to place most reliance on the results obtained by the fluorimetric and scintillation counting methods.

(2) The apparent discrepancy between the two fluorimetric uranium determinations on Bethany (Harvard) is thought to be attributable to the samples having been taken from different parts of the meteorite.

Development of the method

This was accomplished as far as the peroxide separation of uranium and thorium by the use of UX1, a thorium isotope (24·5 day half life). The 0·2 MeV β-radiation from this nuclide is too soft for reliable counting and counts were made on the 2·3 MeV β-particles from UX2. As the period of half growth of this nuclide is only 1·14 minutes, only a few minutes were required for its growth to equilibrium.

Using UX1, it was shown that ether extraction of iron left $100 \pm 2\%$ of the thorium in the aqueous layer. Zirconium was used at this stage as a carrier for thorium. The thorium extraction efficiency as far as the peroxide stage was shown to be between 95 and 100%. Unfortunately, it appeared that the recovery of the uranium was unsatisfactory if zirconium was used as a carrier for thorium; losses of uranium amounted to about 50% and for this reason iron was used as a carrier for thorium.

The investigation of the lead sulphide precipitation technique was made using radiothorium solutions. To avoid contamination from emanating sources, counting was restricted to γ-rays from sealed tubes containing ThB and ThC. Efficiencies of extraction of $100 \pm 2\%$ were obtained.

The overall extraction efficiency for thorium B and C starting with solutions of meteorite-like composition containing thorium was $97 \pm 2\%$. Recoveries of uranium which had been passed through the separation procedure described amounted to $98 \pm 2\%$.

6. Conclusions

By the radon-thoron method, samples of iron meteorites of about 100 g were analysed for uranium and thorium with an accuracy of about 10^{-9} g of uranium and 10^{-8} g of thorium per gram of meteorite. Although the method is less sensitive than the other methods described it has the merit of comparative chemical simplicity and would perhaps be more readily applicable to the analysis of more complex mixtures, e.g. silicate minerals.

Where 30 g samples of iron meteorites are available, analysis of uranium (by the fluorimetric technique) and of thorium (by scintillation counting of the α-particles from ThC) may be made with an accuracy of 3×10^{-10} g and 5×10^{-9} g per gram, respectively. Analysis was restricted to uranium where only 10 g samples were available; an accuracy of about 5×10^{-10} g per gram of meteorite was obtained.

Unfortunately the evaluation of meteorite ages from the analytical data is complicated by the fact that part of the helium content of meteorites is clearly of cosmic ray, rather than of radioactive origin [24]. Under favourable circumstances it is possible to make a correction for the cosmic ray contribution to the helium content, and the corrected value, when coupled with uranium and thorium analyses, may be used to estimate the period which has elapsed since the last solidification of the meteorite. In the case of the Bethany (Harvard) meteorite such a calculation, using the uranium and thorium contents found in the present work, has been made. Assuming that the cosmic ray contribution to the helium has a $^3He : {}^4He$ ratio of 31 : 100 (as found in the meteorite richest in ^3He), Paneth, Reasbeck and Mayne deduced that the helium of radioactive origin

amounts to $0{\cdot}130 \times 10^{-6}$ cc per g; taking the uranium and thorium analyses reported in Table 1, it would appear that the "age" of this meteorite lies between 63 and 91 million years.

Such considerations do not, however, affect the cases of three meteorites (Savik, Ahnighito, Muonionalusta I) whose helium content is below the limit of detection [24]. This apparent absence of helium could have been due either to very low uranium and thorium contents or to extremely recent solidification. The results shown in Table I indicate clearly that the former postulate is incorrect and that these three meteorites must last have solidified not more than 1×10^6 years ago.

Appendix I

Precautions and preparation of reagents

Sodium fluoride. Samples of *Messrs. Merck's* (U.S.A.) and *Messrs. Baker and Adamson's* showed the lowest background fluorescence. Samples of *B.D.H.* sodium fluoride were also used.

Hydrochloric acid. Nitric acid. "Pure" acids from *Messrs. J. W. Towers* were used.

Ether. This was obtained from *Messrs. J. F. MacFarlan.*

Ferric chloride. Uranium and thorium free samples were prepared by ether extraction of ferric chloride from meteorite solutions, after these had been acidified with hydrochloric acid.

Aluminium chloride. Aluminium nitrate solution, acidified with nitric acid, was freed from uranium by ether extraction and from thorium by lanthanum fluoride precipitation. The aluminium was precipitated as hydroxide and the precipitate dissolved in hydrochloric acid.

Barium chloride, distilled water, hydrogen peroxide, 20% caustic soda solution. These were shaken with solid barium carbonate [22] to remove thorium. This method also proved successful for the removal of uranium from these reagents.

Zirconium nitrate. Ether extraction, under normal conditions, was employed to remove uranium. Thorium was removed by lanthanum fluoride precipitation.

Lead acetate. This was obtained from *Messrs. Brady and Martin.*

UX1. Suitable quantities were obtained as follows. Uranyl nitrate hexahydrate was dissolved in water and acid ferric chloride solution added. Ammonium hydroxide was then used to adjust the pH of the solution to 3 to precipitate ferric hydroxide with accompanying UX1 and uranium. The precipitate was digested with ammonium carbonate to rid it of uranium and leave the UX1 behind. The precipitate remaining was collected and dissolved in hydrochloric acid.

Glassware. *Pyrex* glassware, cleaned with boiling nitric acid and distilled water, was used throughout. Solutions were maintained in the acid form as far as possible: this avoided loss of uranium and radium by adsorption on the glass.

Table 2. Uranium and thorium contents of reagents.

Reagent	U $\times 10^{-8}$ g	Th $\times 10^{-8}$ g	*Amount taken*
$AlCl_3$ purified .	$< 1{\cdot}0$	$0{\cdot}7 \pm 0{\cdot}15$	10 mg
$BaCl_2$ purified .	$0{\cdot}7 \pm 0{\cdot}1$	$< 0{\cdot}4$	10 mg
H_2O_2 . . .	$0{\cdot}16 \pm 0{\cdot}17$		20 ml
20% NaOH .	$< 0{\cdot}2$	$10 \pm 3{\cdot}2$	20 ml
HCl conc. . .	$0{\cdot}96 \pm 0{\cdot}32$	27 ± 4	1000 ml

Appendix II

The graphical evaluation of ages from uranium, thorium and helium analyses

If we assume that radioactive decay is the only process causing changes in the uranium, thorium and helium contents of a body, then it follows that an originally helium-free material will have accumulated in a time, t, ending now, a quantity of helium given by

$$N_{He} = 8N_1\{e^{\lambda_1 t} - 1\} + 7N_2\{e^{\lambda_2 t} - 1\} + 6N_3\{e^{\lambda_3 t} - 1\}$$

where N indicates the present-day concentration (in atoms per gram of material) and λ the radioactive disintegration constant; subscripts $_1$, $_2$ and $_3$ indicate uranium, actino-uranium and thorium respectively.

Fig. 5. Nomogram for age calculations. Normalised uranium and thorium contents are obtained by dividing actual values (in 10^{-8} g/g meteorite) by the sum of the helium (in 10^{-6} cc/g), uranium and thorium (in 10^{-8} g/g) values.

Solution of this equation for t is a rather tedious iterative process, and it is much more convenient to use a graphical method. Wickman [23] has proposed such a method and it has been used, and extended, by Jacobi [8] to cover a wider range of ages. We give below an alternative form of graphical solution, which has the advantage that the lines representing the range of possible compositions for a given "age" are now straight, thus facilitating interpolation.

It is clear from the form of the equation given above that, for a given age, the possible values of the uranium, thorium, and helium contents are linearly related, and they can thus be plotted

by the normal method for handling three component systems. Any convenient units may be employed, but for meteorite work it is convenient to adopt 10^{-8} g/g for uranium and thorium, and 10^{-6} cc/g for helium. Having expressed the analytical data in these units, the "normalised" uranium and thorium values are obtained by dividing by the sum of the uranium, thorium and helium values; a line drawn through the point defined by the normalised uranium and thorium values, tangential to the "envelope" curve at the top left-hand corner of the diagram will then intersect the age scale at a value which is the solution of the equation already given. Any convenient range of ages may be covered by suitable choice of units in which to express the analytical data.

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We wish to record our indebtedness to Professor F. A. Paneth, at whose instigation this work was carried out, for many valuable discussions.

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Recent studies on iron meteorites. IV

The origin of meteoritic helium and the age of meteorites

G. R. Martin

Londonderry Laboratory for Radiochemistry, University of Durham

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ABSTRACT

The rate of generation of helium in iron, by nuclear evaporation processes initiated by cosmic radiation, is recalculated with particular reference to the problem of the helium content of iron meteorites. The absence of a significant "depth effect" (postulated by Bauer to arise through the exponential absorption of the primary radiation), is shown to be explicable for small meteorites in terms of helium production by secondary particles (mostly π mesons). Curves are presented showing the calculated helium content as a function of radial distance, and these are in good quantitative agreement with the experimental data of Chackett, Reasbeck and Wilson.

The meteorite (Morden) with the highest known helium content is shown to require a (cosmic-ray flux) $\times$ (time) product about three times the product (present day flux in neighbourhood of earth's orbit) $\times$ ("age" of helium-poorest meteorite, as deduced from radioactive age calculations). This may represent a genuine spread in "ages", although it seems more reasonable to explain it in terms of a theory of cosmic ray production such as Baade and Zwicky's super nova mechanism which would require the mean flux to be several times the flux measured (as to-day) in the absence of an active "local" super nova.

A comparison of the actual sizes of meteorites with the pre-atmospheric sizes necessary to explain the observed helium contents is shown to be in good agreement with the astro-ballistic data of Thomas and Whipple. In particular, the Treysa meteorite, for which observational data are available concerning the fall, provides a most satisfactory test of the present calculations.

1. Introduction

Some five years ago, Bauer [1] and, independently, Huntley [2] pointed out that the present-day flux of cosmic rays in the neighbourhood of the earth's orbit was more than sufficient to produce, through interactions with iron nuclei, the observed helium contents of the iron meteorites during the "ages" assigned to them [3] by the helium-uranium-thorium method. Bauer further suggested [4] that the apparent correlation between mass of meteorite and helium content (in the sense that large meteorites tend to be relatively poor in helium) arose through the exponential attenuation of the cosmic radiation passing through the meteorite. The larger bodies, suffering in general a greater loss by ablation during their passage through the earth's atmosphere, would tend to lose the layers showing the greater helium contents.

Bauer's attempt to give a quantitative explanation of this correlation did not receive universal acceptance, the most serious objection [5] arising from the absence of any well-authenticated radial variation of the helium content of such meteorites as had been examined. In particular, it may be mentioned that the examination of three meteorites (Sacramento Mountains, Toluca, and Thunda) by Wilson [6], and of one (Treysa) by Reasbeck (quoted in reference 7), failed to show any significant depth effect, although on the basis of Bauer's calculations it should have been clearly observable.

However, a recent investigation of the isotopic composition of meteoritic helium, reported in this Journal by Paneth, Reasbeck and Mayne [7], shows in all the samples examined a substantial proportion of ^{3}He. Since this isotope is

hardly likely to have originated in any natural radioactive process, its presence may be taken as confirmation of the essential correctness of the primary assumption of BAUER and HUNTLEY.

Although isotopic analyses have so far been made on the helium from only five meteorites, these were chosen to be as representative as possible, and it therefore seems reasonable to examine at this stage the quantitative implications of the results in the light of our present knowledge of cosmic ray processes. In particular, it seems opportune to re-examine BAUER'S attempt at a quantitative interpretation of the correlation between helium content and total mass of the meteorite in terms of the attenuation of the cosmic radiation passing through it. It may be noted immediately that an element of uncertainty is necessarily introduced into any such calculation by the fact that the average intensity of the primary cosmic radiation in free space during geological time, and the size and shape of the meteorite prior to its fall through the earth's atmosphere must both be deduced from present-day terrestrial observations.

2. CALCULATION OF THE COSMIC RAY PRODUCTION OF HELIUM

We propose first to estimate the rate of production of helium by a beam of cosmic radiation incident normally upon an infinite plane slab of iron, as a function of the depth below the surface of the slab. We shall assume that the energy spectrum of the primary radiation is the same as that deduced for the present-day primary radiation near the earth's orbit, and that the intensity is the same as the present-day intensity per unit solid angle.

BAUER'S calculation [4] was based on an assumed omnidirectional cosmic-ray flux in free space of 1·5 particles/cm^2/sec, absorbed exponentially with an absorption mean free path of 150 g/cm^2 in iron, and producing an average of one helium nucleus per disruption. The basis of such calculations has been greatly altered by the discovery in 1947 by LATTES, OCCHIALINI and POWELL [8] of the π meson. It is now known that π mesons, produced in substantial numbers by the primary particles, are themselves capable of strong interactions with nucleons, and it follows* that a "transition effect" is to be expected; high energy primary particles disappearing as a result of nuclear collisions will give rise not only to evaporation particles (appearing in photographic plates as "stars," some of the "prongs" of which will be helium nuclei) of relatively low energy, but also to π mesons (and some secondary protons) of sufficient energy to initiate further star production—the so-called shower particles. Some of these secondary particles will, furthermore, initiate the production of further showers, and the overall depth dependence of the helium production will clearly be quite complicated. A primary particle which undergoes interaction but is not completely absorbed will, of course, be counted experimentally with the "secondary" particles; there is therefore no necessity to consider the absorption length of the primaries separately from the interaction length. We have assumed, in the calculation which follows, that the original direction of motion of the primary particle is preserved by the subsequent generations; for the higher energy particles, where any deviation would be important,

* The importance of this transition effect became evident to us after a discussion with Professor Sir GEORGE THOMSON in May, 1950.

this is probably sufficiently well assured by considerations of conservation of momentum.

(*a*) *Basis of calculation*

It is our intention to confine this discussion to the meteoritic irons, since only for this class of bodies is there sufficient data to permit comparison with any conclusions which may be reached. Although they may contain up to 15% of nickel, it is sufficient for the present purposes to regard them as composed of pure iron.

The energies of the star-producing particles are well above the Coulomb barrier, and there is good evidence to suggest that the interaction cross section is then almost independent of the nature and energy of the incident particle; under these conditions, the flux of primary particles will be attenuated exponentially, so that at a depth x, the residual primary intensity will be given by:

$$J_1 = J_0 e^{-\mu x}$$

$$\text{where } \mu = Na\rho/A$$

(N is the Avogadro Number, $6{\cdot}02 \times 10^{23}$; a is the effective cross section of the iron nucleus; A is the atomic weight, and ρ the density of iron). The rate of interaction per unit volume of iron will be

$$I_1 = \mu J_1 = \mu J_0 e^{-\mu x}$$

and the rate of production of "evaporation" particles by the primary radiation at this depth

$$N_1 = I_1 Y_1 = J_0 \mu Y_1 e^{-\mu x}$$

where Y_1 is the mean yield of evaporation particles per interaction, which will, of course, depend on the energy spectrum assumed for the primary particles.

These interactions will also produce secondary (shower) particles at a rate given by

$$J_0 \mu S_1 e^{-\mu x}$$

where S_1 is the mean shower particle yield from the interaction of a primary particle with an iron nucleus (assuming the given primary particle energy spectrum). The flux of "first generation" secondary particles at a given depth can be obtained as the solution of a simple differential equation representing the balance between formation of secondaries at the rate given above, and their disappearance, through nuclear interactions, at a rate $I_2 = \mu J_2$. We have thus

$$\frac{\mathrm{d}J_2}{\mathrm{d}x} = J_0 \mu S_1 e^{-\mu x} - \mu J_2$$

which, on integration, and introduction of the boundary condition that $J_2 = 0$ at $x = 0$, gives:

$$J_2 = J_0 S_1 \mu x e^{-\mu x}$$

This flux of secondary particles will similarly give rise to interactions at a rate equal to

$$I_2 = \mu J_2 = J_0 \mu^2 S_1 x e^{-\mu x}$$

and will produce evaporation particles at a rate

$$N_2 = I_2 Y_2 = J_0 \mu^2 S_1 Y_2 x e^{-\mu x}$$

where Y_2 is the mean yield of evaporation particles from the interactions of secondary particles with iron nuclei (assuming now an energy spectrum appropriate to these particles). These interactions will in their turn produce a third generation of energetic particles, with a mean yield, S_2, which can be estimated if one knows the energy spectrum of the secondary particles. The flux of particles representing the nth generation at a depth x can readily be shown to be given by

$$J_n = \frac{1}{(n-1)!} J_0 \mu^{n-1} x^{n-1} e^{-\mu x} S_1 S_2 \ldots S_{n-1} \quad (n > 1)$$

and the corresponding yield of evaporation particles from this generation will be

$$N_n = \frac{1}{(n-1)!} J_0 \mu^n x^{n-1} e^{-\mu x} Y_n S_1 S_2 \ldots S_{n-1}$$

The total rate of production of helium at a depth x will be given by the sum of all such terms as this, multiplied by a factor α, representing the fraction of the evaporation particles which will ultimately yield helium; those particles, that is, which are initially the nuclei of ^{3}H, ^{3}He, or ^{4}He. The yield per gram of iron is thus

$$H(x) = \frac{\alpha}{\rho} \Sigma N = \frac{\alpha}{\rho} J_0 \mu e^{-\mu x} \left\{ Y_1 + \mu x S_1 Y_2 + \frac{\mu^2}{2!} x^2 S_1 S_2 Y_3 + \ldots \right\}$$

It appears from the work of Camerini, Fowler, Lock and Muirhead [9] that the energy spectrum of the secondary particles is more or less independent of the energy of the incident particle; it follows then that the mean yield of evaporation particles, and the mean shower multiplicity will be the same for successive generations, and we can put $Y_2 = Y_3 = Y_4 = \ldots = Y_n$ and $S_2 = S_3 = \ldots = S_n$. We can then simplify the expression for the helium production rate, and find

$$H(x) = \frac{\alpha}{\rho} J_0 \mu e^{-\mu x} \left\{ Y_1 + \frac{S_1 Y_n}{S_n} (e^{\mu S_n x} - 1) \right\}$$

We have neglected in this analysis any contribution from the heavier cosmic ray mesons; these appear to occur with such small yields that no significant error can arise from this omission. An important difference between the behaviour of π mesons in condensed materials and in gases should also be pointed out. The normal fate of a π meson in the atmosphere is not a nuclear interaction, as we have postulated here, but rather decay into a μ meson and a neutrino. The life time of a charged π meson with respect to this decay process is found [10] to be $2{\cdot}54 \times 10^{-8}$ sec, corresponding to a mean decay length of about 10^3 cm for energetic π mesons.

In this distance in air, a nuclear interaction is unlikely, whereas in a solid material it would be virtually certain; this emphasises the danger of using gross atmospheric absorption curves for any calculation of this type. We have also neglected the production of neutral π mesons, since their life time is so short ($\sim 10^{-14}$ sec) that their mode of disappearance will be predominantly decay rather than nuclear interaction, even in a material as dense as iron. The radiations into which these unstable particles are eventually degraded (μ mesons, electrons, high energy photons, etc.) do not give rise to strong interactions with nucleons, and we have felt justified in neglecting any contributions which could possibly arise from them.

Since the various parameters involved in the final expression for $H(x)$ are not all established beyond any possible doubt, we have considered it desirable to indicate in some detail in the following sections of this paper the means adopted to evaluate them. As mentioned before, we propose to carry out this calculation on the basis of the present-day intensity and energy distribution of the cosmic radiation, and to discuss subsequently the validity of this assumption.

(*b*) *The intensity of the primary cosmic radiation, and its distribution in energy*

It appears to be well established that the primary cosmic radiation is composed largely, if not entirely, of positively charged nuclei of very high energy; although estimates vary somewhat, it would appear reasonable to assume that 85% of the primaries are protons [11], and the remainder ^{4}He nuclei, with a contribution from heavier nuclei amounting to about 1%. At the high energies concerned, the nuclear interactions of these particles are more or less independent of their "chemical" nature, and we propose to treat them as though all were protons; it seems unlikely that this assumption will lead to any significant errors.

From an experimental point of view, the problem of deducing an empirical expression for the energy or momentum spectrum of the radiation falls into two parts: the very high energy region where the geomagnetic effects are of little help in analysing the spectrum, and the low energy region (between, say, 1·0 and 15 BeV) in which one can utilise the earth's magnetic field to analyse the momentum spectrum of the primary particles.

In the high energy region, a consideration of the size distribution of extended air showers [12], and of the absorption of cosmic radiation underground [13] has led to general agreement on a power-law spectrum, with an exponent (for the differential spectrum) of about $-2{\cdot}67$; that is

$$F(E)dE \propto \frac{dE}{E^{2{\cdot}67}}$$

This method has been applied only between the energy limits 5×10^{13} to 5×10^{15} eV, and there is unfortunately a large gap between the lower end of this region and the high energy end of the spectrum deduced from geomagnetic effects. It may be noted, however, that this uncertainty is not of major importance, since the number of particles with energies of this order of magnitude is comparatively small.

The low energy region has been investigated by measuring the number flux or the energy flux of the primary radiation as a function of geomagnetic latitude,

λ. An analysis of the effects of the earth's magnetic field on the trajectories of charged particles by Størmer [14], and, later, by Lemaitre and Vallarta [15], has shown that, for a given geomagnetic latitude and direction of approach (defined by zenith angle and azimuth) there is a minimum ratio of momentum to charge for which a particle is permitted to approach the point from infinity. From a consideration of the increase in number flux or in energy flux with increasing latitude, one can thus deduce the momentum spectrum (or, more precisely, if particles of differing charges are considered, the magnetic rigidity spectrum) of the primary radiation. Making suitable assumptions about the mass/charge ratio, the energy spectrum can then be deduced. We have considered three representations of the spectrum, each referring to the flux of particles per cm², per second, and per steradian: (i) an integral form of spectrum, given by Van Allen and Singer [16]:

$$J(>\xi) = \frac{0{\cdot}48}{\xi^{1{\cdot}1}}$$

where ξ is the "magnetic rigidity" (pc/Ze) of the particle, expressed in units of 10^9 volts, (ii) a differential form, due to Neher [17]:

$$F(E)dE = \frac{0{\cdot}048dE}{E^{2/3}(1 + 0{\cdot}09E^{4/3})^{3/2}}$$

where the particle energy, E, is expressed in BeV, and (iii) an integral form, due to Winckler, Stix, Dwight and Sabin [18] (based on the assumption that the primary particles are all protons):

$$J(>E) = \frac{0{\cdot}30}{E^{0{\cdot}90 \pm 0{\cdot}05}}$$

Winckler *et al.*, and Van Allen and Singer deduced their expressions from experimental values of the number flux obtained by counter telescope measurements at various latitudes, and it may be noted that such results, although probably giving the correct form of spectrum, may be expected to give absolute values which are too high, on account of atmospheric albedo. Neher, on the other hand, obtained his spectrum from the differences between integrated curves of ionisation current against altitude at various latitudes, and measured, in effect, the variation of energy flux with λ. Atmospheric albedo will introduce an error in the opposite sense in this case, and we may expect Neher's expression to be low also to the extent that any of the energy of the primary radiation is degraded into energy of non-ionising radiations (especially neutrinos). It is certainly true that Neher's formula gives fluxes which are lower than those given by counter telescope methods by a factor of about 2.

The low energy end of the spectrum is further complicated by the apparent existence of a more or less sharp cut-off in the neighbourhood of 1 BeV; at latitudes higher than about 56°N, where one would expect the flux to be augmented by the permitted access of lower energy particles, no further increase in flux is observed, implying that the primary radiation reaching the neighbourhood of the earth's orbit does not contain any particles of lower energy. Jánossy [19] has suggested

that this cut-off arises from the influence of the sun's general magnetic field, which would impose momentum restrictions similar to those found in the equatorial plane of the earth's magnetic dipole. Unfortunately, data on the general magnetic field of the sun are of doubtful reliability, and it is not certain that this explanation of the cut-off effect is correct; it may well arise from some quite different cause. A recent careful search for Zeeman effects in Fraunhofer lines by von Klüber [20] has, in fact, failed to produce any certain evidence for the existence of a general magnetic field for the sun, although a polar field of 1 or 2 gauss could have been detected; a polar field of about 50 gauss would be required to explain the low energy cut-off. It is not possible to assert, from the available experimental data, that the cut-off is sharp, although for the purposes of our calculation we have assumed that it is, and that no particles of energy less than 1·0 BeV (corresponding to vertical incidence at $\lambda = 55°$N) are present in the primary radiation. We have chosen this value for the cut-off energy because the linear plot of (log flux) against (log energy), which is well fitted by both Winckler's and Van Allen and Singer's data shows a "knee" at this energy. At 1·0 BeV Winckler's spectrum formula gives a flux equal to that found by Van Allen and Singer at 58°N (equivalent to 560 MeV protons at vertical incidence) and by Pomerantz [21] at 69°N (equivalent to cut-off at 32 MeV for protons at vertical incidence; Van Allen and Singer [22] have pointed out, however, that the energy limit in the measurements of Pomerantz is set at about 130 MeV for protons by absorption considerations).

This energy cut-off introduces a further objection to the spectrum proposed by Neher, since the form of it depends, in the low energy region, rather critically on the increase of energy flux between $\lambda = 51°$N and $\lambda = 60°$N. If we accept the existence, from whatever cause, of a cut-off occurring at $\lambda = 55°$N, or thereabouts, then the increment of energy flux observed between 51°N and 60°N has in fact all occurred between 51°N and 55°N. Block 1 of Neher's energy histogram (Fig. 33 of ref. 17) should, therefore, whilst retaining the same area, be placed on a narrower base, thus giving it a height which is probably greater than that of the adjacent block, and calling for a considerable change in the exponent of E in the energy spectrum.

The values obtained by counter telescope measurements during rocket flights by Van Allen and Singer are in good agreement with the spectrum proposed by Winckler *et al.*, based on the better statistics of counter telescope measurements during balloon flights. We have therefore chosen a spectrum of the same form as Winckler's, with exponent for the differential spectrum $-1·95$, cut off sharply at the low energy end at 1·0 BeV, and terminated at the high energy end at 15 BeV. Above this energy we have assumed a higher value for the exponent, $-2·67$, to conform to Hilberry's measurements at much higher energies. The absolute magnitude of the total flux, J_0, we have taken as 0·22 particles per second per cm^2 per steradian, this being roughly evenly disposed between the absolute values obtained by counter telescope and ionisation current methods respectively. It seems unlikely that this value will be in error by more than, perhaps, 20%, and it may be noted, too, that it is in good agreement with an alternative spectrum proposed by Peters [23], which implies a flux (counting only protons) of 0·19

particles per second per cm^2 per steradian. This agrees almost exactly with our assumed value if allowance is made for the presence of about 15% of heavier nuclei in the primary radiation. Our complete differential energy spectrum is therefore:

$$F(E)dE = 0 \qquad (E < 1{\cdot}0 \text{ BeV})$$

$$= \frac{0{\cdot}21dE}{E^{1{\cdot}95}} \qquad (1{\cdot}0 < E < 15{\cdot}0 \text{ BeV})$$

$$= \frac{2{\cdot}57dE}{E^{2{\cdot}67}} \qquad (E > 15{\cdot}0 \text{ BeV})$$

(c) *The interaction cross section of iron for protons and for π mesons*

It seems to be fairly well established that for high energy particles, the heavier elements show a cross section which is more or less independent of the energy and nature of the particle, and only slightly smaller than the "geometrical" cross section of the nucleus. If we take BETHE'S value for the nuclear radius [24] and allow a "transparency" of 20%, which appears to be consistent with recent determinations of this quantity for the heavier elements [25], we arrive at a value for the cross section of iron of $0{\cdot}86 \times 10^{-24}$ cm^2. It corresponds to an interaction mean free path of 108 g/cm^2, or 13·5 cm of iron, and gives a value of 0·074 for μ. We have assumed this to hold for all the high energy particles involved. Since the energies of most of the particles involved are well in excess of m_0c^2, we have neglected energy loss due to ionisation.

(d) *Mean yield of "shower particles" per interaction*

CAMERINI *et al.* [26] have given a graphical representation of a relationship between incident particle energy and shower particle multiplicity, which is of the form

$$S' = 0{\cdot}47(E_i - 0{\cdot}5)$$

where the incident particle energy, E_i, is expressed in BeV. This has been obtained from photographic plate studies, and will presumably make no allowance for any neutron component of the shower particles, which we might expect, on the basis of the usual assumption of the charge independence of nuclear forces, to be about as large as the proton component. If we assume that 20% of the shower particles are protons [27], then we must increase our estimate of the multiplicity by a factor 1·20 to allow for shower neutrons.

The mean yield of shower particles per interacting primary particle will then be given by

$$S_1 = \frac{1{\cdot}20 \times 0{\cdot}47 \int_{E\min}^{\infty} (E - 0{\cdot}5)F(E)dE}{\int_{E\min}^{\infty} F(E)dE}$$

and, using our assumed energy spectrum, we obtain a value

$$S_1 = 2{\cdot}89$$

We have similarly evaluated the shower multiplicity of the secondary particles, S_n, using the form of energy spectrum suggested by Camerini, Fowler, Lock and Muirhead [9], and assuming that this is valid for all generations of secondaries. We have taken a power-law spectrum, with exponent (for the differential spectrum) $-1{\cdot}5$ in the energy range 0·2 to 1·4 BeV, arbitrarily terminated at this energy and replaced, at higher energies, by an exponent $-2{\cdot}5$. We then obtain

$$S_n = 0{\cdot}252 \qquad (\text{for } n > 1)$$

(*e*) *Mean number of "evaporation particles" per interaction**

Camerini, Lock and Perkins [28] have given a graphical representation of the yield of evaporation particles as a function of the incident particle energy. This appears to follow a relationship of the form

$$Y(E) = 7{\cdot}0E^{0{\cdot}36} \qquad (E \text{ in BeV})$$

By integrating the product of $Y(E)$ and our assumed primary particle energy spectrum function, we have derived the mean yield of evaporation particles per interaction,

$$Y_1 = \frac{\int_{E\min}^{\infty} Y(E)F(E)dE}{\int_{E\min}^{\infty} F(E)dE}$$

and obtain a value $Y_1 = 10{\cdot}73$.

Assuming the constant energy spectrum for the secondary particles as before, we have calculated also the value of Y_n. In this case, we have again taken the yield function of Camerini, Lock and Perkins for the higher energy secondaries (above 1·0 BeV) but for the lower energies, where the interactions are essentially elastic, we have assumed the calculated results of Le Couteur [29]. This author has used nuclear evaporation theory to evaluate the yields of various particles as a function of the energy of excitation of the nucleus; where present techniques provide suitable data, his results have been found to be in excellent agreement

*Note added in proof (23 April 1953):

Dr. Goldsack has kindly drawn my attention to the fact that the treatment given in this section does not appear to make adequate allowance for the particles corresponding to the "grey" tracks in photographic emulsions. These "grey" tracks are caused almost entirely by protons of intermediate energies (25–500 MeV), and will not directly contribute any helium. Most of them are brought to rest by ionization energy loss, but some of them, and almost all of the neutrons which may be expected to be produced in equal yield, will give rise to nuclear interactions yielding further evaporation particles.

It appears from a calculation using the empirical data of Camerini *et al.* [9] and the evaporation theory of Le Couteur [29], that the mean number of evaporation particles (due to "grey" protons *and* neutrons) per "grey" proton is just equal to unity, so that the values of Y given above are numerically correct.

These "satellite" stars will occur at a distance of the order of one interaction length from their parent stars, and will thus slightly distort the depth dependence deduced earlier. Although they show a slight tendency to be projected forwards, the emission of the "grey" protons does not exhibit any very strong directional preference. This, coupled with the fact that these particles constitute only 25% or less of the total heavy particle yield, leads us to believe that any such distortion will be negligible in the present connection.

with experiment (see, for example, the data of PERKINS [30]). In this way, we have deduced

$$Y_n = 7{\cdot}82$$

(*f*) *Fraction of the evaporation tracks yielding helium nuclei*

The calculations of LE COUTEUR [29] suggest that about 37% of the total particle yield from "evaporation stars" will be in the form ^{4}He, ^{3}He, or ^{3}H, all of which will be recorded, after a suitable lapse of time to allow the ^{3}H to undergo β-decay, as helium. This is in quite good agreement with the experimental data of BERNADINI, CORTINI and MANFREDINI [31], and of PAGE [32], although these authors, using the photographic plate technique, will have counted ^{3}H among the singly-charged fragments, rather than with the doubly-charged nuclei into which it will have decayed long before the helium measurements on meteorites are made. We have assumed for this ratio

$$\alpha = 0{\cdot}37$$

although it is to be expected that its value will depend to some extent on the mean energy of excitation of the nuclei concerned.

In particular, LE COUTEUR's calculations show that there should be a preference for emission of ^{4}He nuclei at lower nuclear excitation energies, and we must therefore expect that the ratio of ^{3}He : ^{4}He amongst the products will show a similar dependence; it should be noted that the mean nuclear excitation energy will depend on the relative contributions of primary and shower particles to the helium production at any given depth. In smaller meteorites, in which secondary effects would not be fully developed, one might expect a higher relative yield of ^{3}He than in the larger bodies in which the main contribution will have come from the secondary particles. The data given by PANETH, REASBECK and MAYNE [7], in fact show this tendency; the small meteorite, Mount Ayliff, has a ^{3}He : ^{4}He ratio (0·315) notably higher than that of Carbo (0·286); it seems reasonable to explain this difference in these terms, rather than to postulate a large contribution of radiogenic helium in Carbo, which would require a time inconsistent with the time needed to accumulate the cosmic ray helium.

(*g*) *Numerical values*

On inserting into the equation for rate of helium production the values of the various parameters discussed above, we arrive at the following expression:

$$H(x) = 7{\cdot}52 \times 10^{-4} e^{-0{\cdot}074x} \{10{\cdot}73 + 89{\cdot}6(e^{0{\cdot}0186x} - 1)\} \text{ atoms of helium /gFe/sec/sterad.}$$

which is shown graphically in Fig. 1. Fig. 1 also shows the relative contributions to the total helium production by the primary particles, and by the secondaries. The rate of production of helium at the centre of a spherical lump, isotropically irradiated, will show the same dependence on the radius of the lump, and central helium yields, in cc per year, will be given, for a lump of radius r, by

$$1{\cdot}47 \times 10^{-11} H(r) \text{ cc He/gFe/yr/}4\pi \text{ solid angle}$$

3. Comparison with Photographic Plate Data

The value of the intensity used in the calculations of the previous section was essentially a compromise between values obtained by counter telescope methods, and those obtained by ionisation chamber techniques. Neither method makes any assumptions about the cross sections for star production, and it is therefore of especial interest to see how the values now calculated compare with the observations of the rate of star production in photographic plates exposed near the top of the atmosphere. Experiments of this sort have been carried out by Salant, Hornbostel, Fisk and Smith [33], by Addario and Tamburino [34], and by Lord [35].

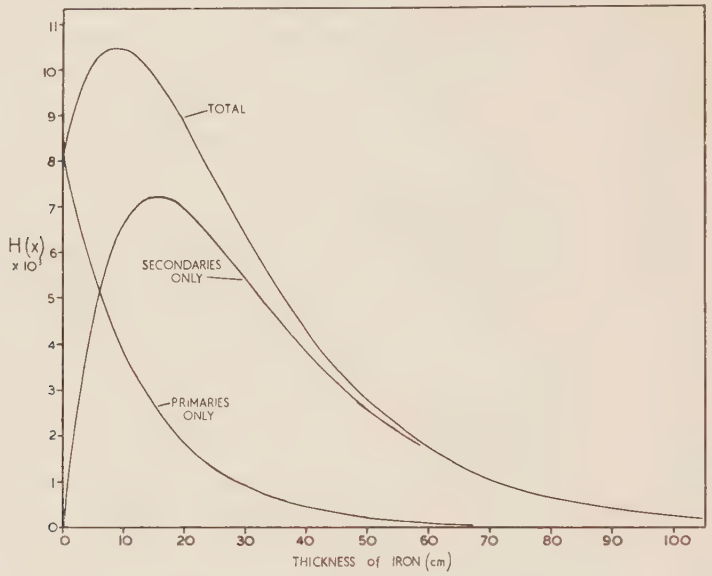

Fig. 1. Rate of helium production, $H(x)$, as function of intervening thickness, x, of iron. $H(x)$ is expressed in atoms of helium produced per g of iron per second, under irradiation from unit solid angle by cosmic radiation of present-day quality and intensity.

We have calculated the rate of star production to be expected on the basis of our assumptions, making due allowance for the fact that silver bromide (average atomic weight 95) will have a somewhat smaller cross section per g than iron (atomic weight 56). Lord's plates were exposed at $\lambda = 55°$N, and the flux of primary particles reaching them will have been subject to modification by the magnetic field of the earth. Alpher [36] has correlated the work of Størmer, Vallarta, and others, and presented the available data on the geomagnetic effects in a convenient graphical form. Using his curves relating the minimum energy of approach to the zenith angle and azimuth at various geomagnetic latitudes, we have calculated the average flux (assuming our adopted energy spectrum) as a fraction of the flux at vertical incidence at the same latitude. For $\lambda = 55°$N, we find

$$\varepsilon_{55°} = (\bar{J}/J_0)_{55°} = 0{\cdot}641$$

In this calculation we have assumed that penumbra effects are negligible, and used the simple Størmer cone, modified by the earth's shadow effect. After making these corrections, we would predict the production of stars in photographic emulsion at the rate of 2360 stars per cc per day at the top of the atmosphere at latitude 55°N. This may be compared with the value of 2390 stars per cc per day found experimentally by Lord, and, although the closeness of the agreement is certainly fortuitous, it may be taken as confirming the essential correctness of our choice of data. The value obtained by Lord is slightly higher than those of the other two sets of workers, and we have taken this value for purposes of this comparison, since errors in measurements of this type mostly tend to reduce the number of events recorded (for example, any faults in the preparation or development of the plates, or inadequate scanning of the developed plates).

4. The Ages of Meteorites

(*a*) *Modification of the helium-uranium-thorium method*

It is clear that the presence of substantial amounts of cosmic ray produced helium will alter considerably the "ages" assigned to meteorites on the assumption that all the helium had been produced in the course of the decay of the natural radioactive elements present as traces in the iron. If one could confidently assert the constancy of the ratio of ^3He : ^4He in the helium produced by cosmic rays, then a correction, simple in principle, if somewhat uncertain in practice, could readily be made to the total helium content to enable the "ages" to be calculated as before. As pointed out before, however, it is clear from the calculations of Le Couteur that this ratio is dependent to some extent on the mean energy of excitation of the nuclei involved, and this will certainly depend on the relative contributions of primary and secondary particles to the total helium production at the point in question. For meteorites in which the bulk of the helium is of cosmic ray origin, it seems unlikely that this correction could be applied with sufficient assurance to give radioactive age determinations of any precision.

For samples which were once largely screened from cosmic ray influence by an extensive outer layer lost during passage through the atmosphere, these arguments lose much of their force; one might expect that the ^3He : ^4He ratio will be more or less stable, since most of the cosmic ray production of helium in so large a body comes from the secondary particles. Present results seem to indicate a value of about 0·29 for the ratio. The quantity of cosmic ray produced helium will also be so much smaller that its subtraction could be effected with comparatively little uncertainty. Paneth *et al.* [7] have in fact utilised this argument in the case of the Bethany (Harvard) meteorite, for which they deduced an age of 75×10^6 years. It may be noted that the minimum helium content recorded for a meteorite* ($0{\cdot}15 \times 10^{-6}$ cc/g for Bethany Goamus) would represent about the same age as that quoted for Bethany (Harvard) by Paneth *et al.* if this helium were all of

* We neglect here the three meteorites (Savik, Ahnighito, and Muonionalusta; see below) which contain no detectable helium at all. They are clearly different in kind from the generality of meteorites, and require separate discussion.

radiogenic origin. It is clearly desirable to examine more meteorites of the helium-poor type in order to provide a more satisfactory statistical basis for a statement as to their age, but it seems unlikely that any radical changes are to be expected.

(*b*) *Magnitude of the cosmic ray contribution*

The helium-poor meteorites may be assumed to be deficient in helium not on account of a shorter time of exposure to the cosmic radiation, but rather because their present masses were shielded during their exposure to the radiation by an outer layer which was removed during their flight through the atmosphere. The "transition effect" ensures, however, that a small body will receive almost uniform irradiation, and we may therefore take the helium content of the helium-richest meteorites as roughly indicative of the helium production to be expected in an unscreened body exposed to the radiation. It is of interest therefore to consider the time which would be required, on the basis of the rate of production deduced earlier, to accumulate the helium content of Morden ($38{\cdot}1 \times 10^{-6}$ cc/g), the highest so far recorded. This works out to be $2{\cdot}52 \times 10^8$ yr and in this time the contribution of the natural radioactive substances would have been quite negligible by comparison. It is striking that only a factor of 3 separates the ages of the helium-richest meteorite (on the basis of production of the helium by cosmic rays) and of the helium-poorest one (calculated by the radioactive age formula after making allowance for cosmic ray contribution). One is tempted to draw the conclusion that a more satisfactory explanation would be to postulate a "catastrophic" origin for the meteorites, about $0{\cdot}75 \times 10^8$ years ago, and to couple this with a mean cosmic ray flux of about three times the present-day intensity. The varying helium contents would then be explained in terms of varying amounts of shielding from cosmic radiation during this time.

This still provides no satisfactory explanation for the three meteorites (Cape York, Savik; Cape York, Ahnighito; and Muonionalusta) found by Paneth and his co-workers to contain no helium, within their limits of detection. These three can only be assumed to have solidified not more than 10^6 years ago, and thus cannot be fitted into the same scheme as the other meteorites; one is forced to postulate some additional mechanism in these cases—the most probable would appear to be re-melting by passing close to the sun. It would be most interesting to examine the helium isotope ratio of the other two Cape York meteorites ("Woman" and "Dog"), which do contain a measurable amount of helium; if these bodies are genuinely associated (and one cannot exclude the possibility that they are not), then one might expect to get from them a true measure of the cosmic ray produced helium isotope ratio, since they appear to be so "young" that little radioactive helium could have accumulated.

The cosmic ray flux to which the meteorites have been exposed may have been greater than at present experienced on the earth for one or both of two reasons: (i) if the low energy cut-off observed in the terrestrial energy spectrum is in fact accounted for by the magnetic field of the sun, then at the greater solar distances at which the meteorite spends most of its time (it may be expected that a meteorite will have a fairly strongly elliptical orbit) this cut-off will occur at lower energies, thus raising the total incident flux.

It must be recorded that there is little definite evidence for or against such an hypothesis, and the lower part of the energy spectrum is subject to so much uncertainty that it is virtually impossible to make any useful extrapolation to lower energies. One important point may however be noted: in section 5 of this paper it will be shown that the depth dependence of the helium content of those meteorites so far examined is in excellent agreement with the assumptions so far made. If a significant portion of the flux needed to bring the ages into alinement is to be obtained by a reduction of the low-energy cut-off, this will considerably distort these calculated curves, since the particles of low energy will produce very few secondaries, and will, furthermore, be absorbed more rapidly in passing through the meteorite, on account of energy loss through ionisation. The fact that we have sensible agreement between the depth dependence calculated on the basis of our assumed energy spectrum, and that found experimentally, is therefore a strong argument against the presence of a significant low energy component of the cosmic radiation which is cut off from the earth by the magnetic field of the sun. The recent work of VON KLÜBER, already mentioned, also makes this appear an unlikely explanation.

It may be objected that the complete absence of low energy particles is, *a priori*, unlikely. Two explanations may be advanced to account for this absence, however: in the first place it is possible that the generating mechanism for the cosmic radiation either does not produce low energy particles, or (possibly through an associated magnetic field) does not allow them to escape from the neighbourhood of the source. In the second place, it should be observed that particles whose origin is truly cosmic (and the apparent isotropy of the radiation reaching the earth argues in favour of such an origin) will reach the earth only after passing through a significant thickness of interstellar matter. This will have the effect of reducing the energy of all the particles, but the energy loss relationship is such that the slower particles lose energy faster than the more energetic particles, with the result that the spectrum would be more or less strongly biased against those with lower energies.

(ii) The mean flux during geological time may well have been greater than it is at present, as has been postulated by READ [37] in an attempt to explain the helium content of beryls. The only experimental evidence on this point relates to the concentration of ^{14}C in the atmosphere, seas, and biosphere, which has been investigated by LIBBY [38]. It appears from LIBBY's calculations that the observed ^{14}C concentration can be accounted for quite well in terms of its production (through the $^{14}N(n, p)^{14}C$ reaction) by a neutron flux equal to that secondary to the present-day cosmic ray flux. This apparent agreement, however, can only be used in support of arguments about the cosmic ray flux during the past 5,000 years or so, since the present ^{14}C concentration is rather insensitive to the rate of production more than about one half-life ago.

The theory of BAADE and ZWICKY [39] on the origin of cosmic rays in super novae, which has been elaborated by HOYLE [40], would, however, demand just such a difference between the present-day level of activity (there has been no super nova outburst within the Galaxy sufficiently recent to influence the present flux) and the mean level over a very long period of time. HOYLE suggests that an

average of only, perhaps, one super nova outburst in ten meets the angular momentum requirements of his theory of cosmic ray production, and on this basis he is able to show that the present cosmic ray flux is consistent with the estimated rate of occurrence of super novae (favourable and unfavourable) of about one per galaxy per 500 years. Hoyle has further shown that the mean level of cosmic ray activity would be significantly disturbed only by the occurrence of a suitable super nova outburst within the Galaxy; such an event in even the nearest extra-galactic nebula would be too distant to raise the level by a significant amount. Within the Galaxy, however, it would appear from Hoyle's calculations that the occurrence of a cosmic ray producing super nova once every 5,000 years on the average would raise the mean cosmic ray intensity by a factor of about 6. There is clearly a large margin of error in any estimate of this sort, but if one assumes a mechanism of this type, then it follows automatically that the level of intensity will be raised by a considerable amount during isolated short periods of time by the occurrence of such local events; the present-day estimate of the level of intensity is then almost certainly an underestimate of the true mean level.

5. Depth Dependence in a Spherical Model

It will be apparent from the discussion in the previous section that the radiogenic contribution to the total helium content of most meteorites is comparatively small, and we propose for the purpose of estimating the depth dependence to neglect this more or less constant addition to the cosmic ray produced helium. To perform such a calculation, it will be evident that one needs to know the distance from the selected point to the surface of the original pre-atmospheric mass, as a function of suitable coordinates. Clearly any rigorous calculation along these lines will be impossible, not only on account of the difficulty of dealing with bodies of an irregular shape, but also because one does not know the shape of the original mass, or the orientation of the post-atmospheric mass within the original body. As Bauer has pointed out, however, a compact shaped body will not deviate in its behaviour too much from that of a sphere, and we have taken as a model for purposes of calculation a sphere, subject to uniform ablation during its passage through the atmosphere, so that the centre of the original sphere remains central. Actual meteorites will clearly deviate more or less grossly from this idealised model, and this must be borne in mind when considering the agreement between prediction and experiment.

Even for a spherical model, the calculation of the depth effect is tedious, each point along a radial path involving individual graphical integration. Fig. 2 shows the results of such a calculation, using the relationship shown graphically in Fig. 1, and carried out for masses with pre-atmospheric radii of 10, 15, 20, 30, 40, 50, 60, 80, 100, and 150 cm. The absolute magnitudes of the curves have been adjusted so that the meteorite showing the highest known helium content (Morden, about 4 cm post-atmospheric radius, with $38{\cdot}1 \times 10^{-6}$ cc He/g) is included. It will be clear from this diagram why little or no radial dependence of the helium content was observed with Treysa (central helium content 26×10^{-6} cc/g) or Thunda (central helium content $30{\cdot}3 \times 10^{-6}$ cc/g), if one bears in mind that only 8 cm and 6 cm radial distances were respectively available. Recent work in this

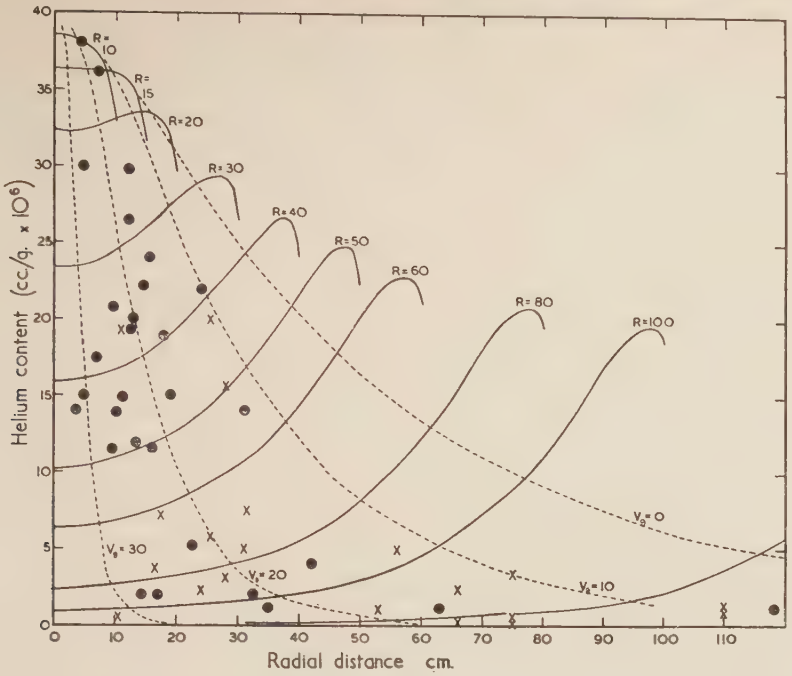

Fig. 2. Helium production in iron spheres of various initial radii (R, in cm) as a function of radial distance (solid lines). Broken lines represent surface helium content as function of post-atmospheric radii, for various geocentric velocities (V_g in km/sec) with $\sigma = 1{\cdot}25 \times 10^{-12}$ g/erg. Solid circles: data for single-fall meteorites. Crosses: data for meteorite showers. (Helium contents have been taken from Table 4 of the preceding paper by Chackett, Reasbeck and Wilson, [41]: radii have been deduced from the masses quoted in the "Catalogue" of Prior [42].)

laboratory has, however, shown a definite decrease in helium content with increasing distance from the surface of the Carbo meteorite*. In Fig. 3 we have plotted the available measurements on Thunda (by E. J. Wilson [6]), Treysa, and Carbo† (both by P. Reasbeck) as a function of radial distance, superimposed upon curves representing the calculated helium contents for spherical masses of such pre-atmospheric size as would give the observed central helium content. It will be seen that the agreement is as good as could be expected in view of the assumptions implicit in this comparison. We have not included Sacramento Mountains or Toluca (for which data were obtained by Wilson [6]), since they are not of a shape suitable for comparison with the present calculated data; Sacramento Mountains

* It may be noted that it is extremely difficult to obtain samples from the central portions of large meteorites, and this work would not have been possible were it not for the kindness of Dr. C. Frondel of the Geological Museum, Harvard University, who provided this laboratory with the necessary samples. The analyses on these are not yet complete, and the values used in the preparation of Fig. 3 are preliminary values.

† Carbo is a somewhat non-spherical meteorite (having rather a conical shape), and the helium content cannot be expected to follow exactly that predicted for a spherical lump. Allowance for this has been made in the following way: the "centre" of the original mass has been assumed to be at the point along the bore-hole (roughly along the axis of the cone) where the minimum helium content was found. Distances from this "centre" have been uniformly scaled down in the ratio (actual distance from this centre to the present base of the cone) : (radius of a sphere of mass equal to the present mass). This involved a reduction by a factor of 0·858.

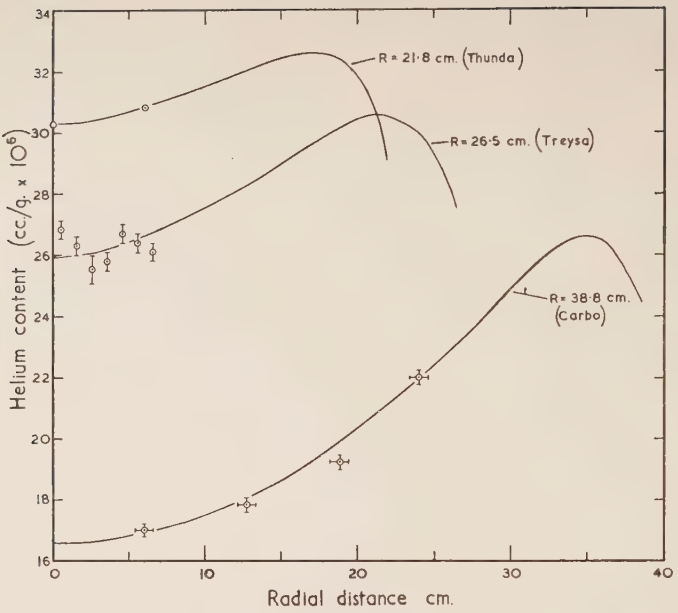

Fig. 3. Comparison of calculated "depth effect" with experiment. The data obtained by Chackett, Reasbeck and Wilson [41] for Thunda, Treysa, and Carbo are shown (experimental points) together with curves calculated to give the observed central helium content for these three meteorites.

meteorite is a long, almost cylindrical mass, and Toluca is one component of a meteorite shower for which one can have no orientational data whatever.

6. Loss of Mass on Passage through the Atmosphere

The kinetic energy of a meteorite approaching the earth with the smallest possible velocity (the "velocity of free fall", equal to 11·1 km/sec) is considerably in excess of the energy necessary to vaporize the whole mass ($6{\cdot}1 \times 10^{11}$ ergs/g compared to the estimated energy needed for vaporization, 9×10^{10} ergs/g). It is likely, therefore, that a meteorite, especially one which has a geocentric component of velocity in addition to the velocity of free fall, will suffer some considerable loss of mass by evaporation, or, at least, by melting, during its passage through the atmosphere. It seems to be fairly well established that a meteorite will only survive the impact on landing if it has been slowed down to a velocity of the order of its limiting velocity before it reaches the earth; those which are not sufficiently retarded will almost certainly be destroyed upon impact. It is therefore important in the present connection to obtain an estimate of the probable loss of iron by ablation during the descent through the atmosphere.

Whipple [43], following the work of Hoppe [44], has shown that the terminal mass and velocity of a *meteor* are related to its pre-atmospheric mass and velocity by

$$m = m_0 \exp\left\{\sigma \frac{v^2 - v_0^2}{2}\right\}$$

where

$$\sigma = \frac{\Lambda}{2\Gamma\zeta}$$

and Γ, the drag coefficient, is defined by

$$\text{Drag} = -\Gamma d v^2 \mathfrak{U}$$

and Λ, the heat transfer coefficient, by

$$\text{Heat transfer} = -\Lambda d \frac{v^3}{2} \mathfrak{U}$$

In these equations, d is the local density of the air, v the instantaneous value of the meteor velocity, $\mathfrak{U}$ the cross-sectional area of the meteor, and ζ the energy needed to remove, by melting or evaporation, as appropriate, one gram of material from the initially cold, solid, meteor.

Whipple and his collaborators have made extensive investigations of the luminosity of meteors, from which values of σ may be deduced. It appears that, although there is a fair variation in the values of σ observed, there is no appreciable correlation between σ and velocity or air density [45]. It seems possible, however, that the great bulk of the observed meteors are not of the same nature as iron meteorites, but are rather composed of poorly sintered masses of interstellar dust [45]. In this case, one might expect that a more tightly bound iron fragment would have a rather greater value for ζ, and hence a smaller value for σ, than the average value, $1{\cdot}8 \times 10^{-12}$ g/erg, found for meteors.

It would seem reasonable to divide the path of a meteorite through the atmosphere into two regions: an upper portion in which "molecular flow" conditions may be expected to hold, with the meteorite surface being bombarded by individual gas molecules, and where evaporation would be expected to be the appropriate mode of loss of mass; and the higher pressure region where viscous flow conditions would certainly obtain, and mass loss would be predominantly by melting (the molten layer would be instantly blown away) rather than by evaporation. In the upper region (which would be rather unimportant for a large meteorite), Whipple's meteor data could probably be applied with little modification. There are very few data on which one could base predictions in the higher pressure regions for such velocities as are relevant in the present connection. Thomas and Whipple [45], however, have reported experiments with solid carbon dioxide in a wind tunnel, and with Woods metal projectiles in a controlled pressure free flight range, and it would appear from the data they present that Λ has a value under these conditions of about 0·015. If we take the generally accepted value of 0·5 for Γ, and $1{\cdot}2 \times 10^{10}$ ergs per g for ζ (corresponding to melting of the iron), then we arrive at a value of $1{\cdot}25 \times 10^{-12}$ g/erg for σ. This is well within the range of values found by Whipple and his collaborators for meteors, and it would appear reasonable to apply this value over the whole of the meteorite's trajectory. Using this value of σ in Whipple's relationship for the terminal masses of meteorites, and assuming that the terminal velocity of a recoverable meteorite is negligible in comparison with its initial velocity (indications are that limiting velocities for

iron spheres are of the order of 1 km/sec), then we can deduce, for a given initial velocity relative to the earth, what will be the ratio of final to initial masses, or, assuming again a spherical model, the ratio of final to initial radii. Table 1 gives values for these ratios for a number of possible geocentric velocities; the terrestrial velocity is related to the geocentric velocity nearly enough by the relationship

$$V^2 = V_g^2 + 124{\cdot}9 \ (V \text{ and } V_g \text{ in km/sec})$$

Table 1. *Mass ratio, and radius ratio, for spheres of various geocentric velocities, subjected to uniform ablation during passage through the atmosphere.* σ *taken as* $1{\cdot}25 \times 10^{-12}$ g/erg.

Geocentric velocity km/sec	*Terrestrial velocity km/sec*	*Mass ratio*	*Radius ratio*
0	11·1	0·462	0·773
10	14·9	0·246	0·626
20	22·9	0·048	0·364
30	32·1	0·00166	0·118
40	41·6	2×10^{-5}	0·027

We have shown in Fig. 2 lines which represent, for a given geocentric velocity, the maximum helium content as a function of post-atmospheric radius, assuming a spherical model. We have also plotted on this diagram points which represent the helium contents and equivalent radii (assuming spherical masses of density 8·00 g/cc) of such meteorites as have been examined. We have assumed here that the sample analysed for helium was taken from near the present crust of the meteorite; in many cases this was certainly so, and the difficulty of acquiring samples from the inner parts of large meteorites prompts us to suggest that it will generally be safe to assume that these samples have been taken from within a few centimetres of the outer surface. In any event, the variation of helium content with depth is not great enough to introduce serious errors. On this diagram, a solid circle indicates a meteorite which appears from the available information to have been either a solitary fall, or at most, a large mass accompanied by a few smaller fragments. We have included for comparison the available data on meteorites which are thought to have been components of showers; if one assumes that these meteorite showers represent the break-up of a much larger mass either on entering the earth's atmosphere, or possibly, on coming within the limit of stability set by the earth's gravitational field (the Roche limit), then the validity of these points is open to question, since one has no method of estimating the stage at which this break-up occurred, and the orientation of the surviving fragments within the original mass is completely unknown. On the other hand, these fragments may simply have been pursuing closely similar orbits, and not have been very effective in providing mutual screening during their cosmic ray irradiation. The points marked with crosses must at least be regarded with some reserve.

It will be noted that there are no points on this diagram corresponding to velocities less than the minimum velocity of approach, which would represent zero geocentric velocity for the meteorite in free space. There are, in fact, no points corresponding to geocentric velocities less than 10 km/sec, and it may be noted that Thomas and Whipple have estimated that the minimum velocity of approach of an asteroid with perihelion distance less than 1 A.U. would be about 12 km/sec. If the generality of meteorites are pursuing orbits similar to those of the asteroids, then this is a very satisfactory concordance.

An analysis of the apparent velocities of the meteorites included in this comparison shows a mean geocentric velocity of 21 km/sec with standard deviation 5 km/sec. Recent work on radar reflections from the trails of shower meteors has also yielded velocities of about this magnitude, and this may be taken as evidence that the meteorites examined were in fact periodic. It should be pointed out, however, that this must not be used as evidence against the existence of meteorites with velocities in excess of the parabolic limit, since such meteorites would be almost completely destroyed during their passage through the atmosphere. Although the meteorites examined were a random selection of those available, it must be acknowledged that a natural bias against small meteorites will be introduced by (a) the smaller probability of recognition of smaller masses as meteoritic, and (b) the greater reluctance of museum curators to break up small complete meteorites.

Fortunately, a more precise check than this is possible. For the Treysa meteorite, Wegener [46] has collected the accounts of a large number of eye-witnesses of the fall, and has deduced a trajectory for the meteorite, which, incidentally, led to its subsequent recovery [47]. He deduced a geocentric velocity of 16·3 km/sec, equivalent to a terrestrial velocity of 19·8 km/sec, and, although this is necessarily subject to a substantial margin of error, it is interesting to note that such a velocity would result in a reduction in radius by a factor of 0·446. The central helium content of Treysa would indicate, on the basis of the present calculations, an initial radius of 26·5 cm, and reduction by this factor would give a post-atmospheric radius of 11·8 cm. The recorded mass of Treysa is 63 kg, corresponding to a radius of 12·2 cm, which again may be taken as in surprisingly good agreement with theory. It may be noted that Treysa is a comparatively compact mass, not far from spherical in shape, and should thus provide a particularly satisfactory model on which to test the calculations outlined earlier.

7. Conclusions

It will be clear that the foregoing calculations are dependent to a certain extent upon data, some of which are not yet established beyond dispute, and they cannot be regarded as in any way final. It would appear, however, that such checks as are possible show that the theory is nowhere inconsistent with the best experimental data, and it would seem reasonable to conclude that no gross uncertainties remain.

The present evidence thus suggests that all but three of the iron meteorites so far examined were formed in some process of a "catastrophic" nature at a time about 75×10^6 years ago; that they have been subject since then to a flux of

cosmic radiation of the same quality as the radiation at present reaching the neighbourhood of the earth's orbit, but, on the average, of about three times the present intensity. The absence of any significant "depth effect" in small meteorites is consistent with the transition effect to be expected in the cosmic radiation, and the calculated effect is in good agreement with the observed radial dependence of the helium content of the only large meteorite available for examination. The post-atmospheric sizes and helium contents of the iron meteorites can be interpreted in terms of the astroballistic theories of Thomas and Whipple; in one specific case (Treysa), for which velocity data are available, the agreement between experiment and theory is excellent. The three apparently helium-free meteorites cannot be explained by means of the present hypotheses, and it is necessary in these cases to invoke some additional postulate, such as a recent re-melting, or even a more recent "formation" separately from the remainder of the meteorites.

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CORRECTIONS

The Use of Ionization Potentials: L. H. Ahrens.

Part 1. Ionic radii of the elements, 1952, Vol. 2, pp. 155 to 169. In the equation relating I and Z (p. 162) the exponent 2 has inadvertently been placed on I; the equation should read, $I \alpha Z^2$. In the last line on p. 167, 3·5 should read 0·25.

Part 2. Anion affinity and geochemistry, 1953, Vol 3, pp. 1 to 29. The value of $\Delta_{2,3}$ for Ge (Table 12, p. 26) should be 18·3 volts and not 17·3 volts.

Obituary

Professor Paul Niggli
1888–1953

With the passing of Paul Niggli, Professor of Mineralogy and Petrography at Zürich, science loses one of its outstanding figures, a brilliant investigator of untiring energy and great versatility, who ranged in his researches through whole fields of crystallography, mineralogy and petrology, inspired by a conception of their essential unity which in his own example, was the ultimate goal of achievement.

Niggli was born at Zofingen in Canton Aargau and graduated at the Eidgenössische Technische Hochschule in Zürich in 1907.

His doctoral dissertation carried out under the supervision of Grubenmann dealt with the chloritoid schists of the northeast edge of the Gotthardmassif (1912), and provided a pioneer study applying physico-chemical principles to the subject of stress metamorphism.

He shared indeed with V. M. Goldschmidt, who a year earlier had published his classic study on contact metamorphism, the credit of the first application of the phase rule to the study of mineral assemblages in metamorphic rocks.

From these endeavours he proceeded as guest investigator in 1913 to the Geophysical Laboratory in Washington, and there engaged in experimental studies in silicate systems with volatiles, collaborating also with his Washington colleagues, Johnston and Morey, in a critical survey of problems of metamorphism and the hydrothermal synthesis of silicates.

Soon after his return to Zürich, he was appointed to a Chair at Leipzig, moving to Tübingen in 1918.

This period saw the production of his *Geometrische Kristallographie des Discontinuums* (1919) in which he set himself the task of bringing up to date Schönflies's *Krystallsysteme und Krystallstructur* (1891) in the light of the results then developing from the new study of x-ray analysis. In this treatise he provided the idea of a systematic deduction of the space group by means of x-ray data, and supplied the outline of methods which have since been used for their determination.

Niggli's early interest in systems with volatile components led to his theoretical treatment of their behaviour in magmas, published as a Leipzig *Preisschrift* in 1920. He was later to elaborate these studies in his book *Das Magma und seine Produkte* (1937) of which only the first volume appeared.

In the field of igneous petrology he was particularly active in the study of petrographic provinces, and he devised a system of calculations (Niggli values and molecular norms) for the treatment of rock analyses to clarify trends of variation. These devices have obtained considerable vogue on the Continent but have not been widely used in Britain or the United States. They were given full play in the two monumental memoirs he produced with Burri on *Die jungen Eruptivgesteine des mediterranen Orogens* (1945, 1948), a title which scarcely reflects the scope of the wide survey attempted of the ophiolites and post-ophiolitic eruptives ranging from Europe to the western borders of the Pacific.

His interest in the tectonic association of magma types had long been evinced, for as early as 1922 in *Der Taveyannazsandstein und die Eruptivgesteine der jung mediterranen Kettengebirge*,

he had extended the then prevalent division of igneous rocks into Atlantic and Pacific Suites by recognising a third Mediterranean Suite typified by the potassic Roman province in its tectonic setting on the borders of the Apennine chain.

His surveys were extended into the realm of ore deposits of which he provided a genetic classification based in part on their igneous and tectonic associations (1929).

With GRUBENMANN whom he had succeeded as Professor at Zürich in 1920, he produced in 1924 the first volume of a treatise on metamorphism, as a successor to the classic *Die Kristallinen Schiefer*. In this the general principles of the subject were presented, but the projected second volume, which was to provide a systematic classification, never appeared, though he supplied later a skeleton revision of GRUBENMANN's original chemical divisions of the metamorphic rocks.

His brilliant survey of the metamorphism of the Swiss Alps (1950) was his last published investigation in this field.

NIGGLI's contributions to Swiss mineralogy are enshrined in the two volume *Die Mineralien der Schweizeralpen* (1940) which he wrote in collaboration with KOENIGSBERGER and PARKER; it ranks without doubt as the finest topographic mineralogy in existence.

Among his numerous textbooks his *Lehrbuch der Mineralogie* originally published in 1920, set a new standard of achievement, and provided a new vista of the range of modern mineralogy, testifying to his own conviction of "Mineralogie als der Kitt . . . . der die verschiedenen Disciplinen der mathematisch-naturwissenschaftlichen Facultät zusammenhält." The book ran to three editions and broadened in scope to include an extended treatment of crystal chemistry.

Succeeding GROTH as editor of the *Zeitschrift für Kristallographie*, he served in that capacity from 1921 to 1940, in later years with VON LAUE, EWALD and FAJANS as co-editors.

Under his direction the *Zeitschrift* expanded to a truly international journal, and after the War he acted, from its inception, as a member of the advisory board of *Acta Crystallographica*, and in like capacity, of this present journal.

NIGGLI played a prominent part in the administration of the Technical High School and of the University of Zürich. He served for periods as Rector of each of these institutions and he was for many years president of the Swiss Geotechnical Commission, widening its activities and instrumental in forging a closer link between the geological sciences, technology and industry.

He was the recipient of many honours both at home and abroad. The Roebling Medal of the Mineralogical Society of America was awarded him in 1947 and in the following year his sixtieth birthday was celebrated by the appearance of a *Festschrift* containing original contributions of many of his colleagues and former students.

He died suddenly in Zürich on January 13, 1953.

C. E. TILLEY

Methods of Genesis of Clays and Related Minerals

will be the theme of the Clay Minerals Conference to be held at the University of Missouri, Columbia, Missouri, on 15–17 October, 1953. Particular attention will also be given to methods of distinguishing between kaolinite and chlorite. The Conference is sponsored by the National Clay Minerals Committee, the University of Missouri and the Kansas Geological Survey.

Anyone interested in presenting a paper on the above theme or on clay mineralogy, technology, physical behaviour of clays, techniques of mineral determination, origin of soils, clays in soils, origin and distribution of clays in soils, clays related to ore deposits, and allied topics, please write Mr. A. F. FREDERICKSON, Washington University, St. Louis, Missouri. A detailed programme, including field-trip information, will be available on request in August, 1953. Everyone interested in any aspect of clay mineralogy or technology is cordially invited to attend the Conference.

Symposium on Geochemistry, Zürich, 1953

Mineralogisch-petrographisches Institut.
Eidg. Technische Hochschule.

August 11, Tuesday, 9 a.m.

Opening speech by the acting president, Michael Fleischer of the U.S. Geological Survey. Introduction by the local chairman, C. Burri, Eidg. Technische Hochschule, Zürich.

The day will be devoted to the Problem of Organizing and Making available Geochemical Data, in particular the organization of current compilations of regional analytical data.

9.45 a.m.

Kalervo Rankama: Opening remarks on compilation, revision, and organization of geochemical data.

Earl Ingerson: Geochemical work of the Geochemistry and Petrology Branch, U.S. Geological Survey.

Michael Fleischer: Revision of Bulletin 770, Clarke's "Data of Geochemistry".

Marjorie Hooker: Progress report on the revision of Professional Paper 99, Washington's "Chemical Analyses of Igneous Rocks".

Wolfgang Müller: Der Gmelin-Informationsdienst als Schrifttumsarchiv für das Gebiet der Geochemie (Gmelin-Institut, Clausthal-Zellerfeld).

Wolfgang Müller: Die Geochemie im Gmelin-Handbuch (Gmelin-Institut).

Luncheon

2.15 p.m.

Paul Rosbaud: The publication of geochemical papers in Geochimica et Cosmochimica Acta. (Pergamon Press, London).

S. I. Tomkeieff (Newcastle-on-Tyne): Periodic system in geochemistry.

S. I. Tomkeieff: Petrochemistry and petrogenesis.

August 12, Wednesday, 9 a.m.

Short reports from various geochemical centres. Thus far about 20 titles have been submitted mostly from European research centres. It will be concluded by a summary by T. F. W. Barth: Current geochemical research in the world.

Excursion

Subsequent to the Symposium an excursion into the Eastern Gotthard Massif (alpine metamorphic rocks) lasting $1\frac{1}{2}$–2 days will be carried out. Prospective participants are asked to communicate with Professor Conrad Burri, Mineralogisches Institut E.T.H., Zürich 6 (Switzerland) Sonneggstr. 5, who will be glad to give all desired information. Likewise questions concerning hotel accommodation, and other practical questions should be addressed to Professor Burri.

INFORMATION FOR CONTRIBUTORS

I. GENERAL

1. Papers on Geochemistry should be submitted to the editors for the appropriate country or language (*Papers on Cosmochemistry should be sent to Prof. F. A. Paneth, F.R.S.*). Papers submitted for publication will naturally be judged from the standpoint of scientific originality and novelty. Technical details of apparatus used in scientific investigation can, however, be presented in brief notes. The preparation of progress reports and review articles will be invited by the Editors from time to time and it is therefore requested that no uninvited contributions of this nature be submitted. The Journal will appear as independent and complete numbers, which will be sold separately and combined into volumes of about 300 pages.

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3. Authors will receive 75 free reprints of their papers. Additional copies can be purchased if ordered at the time the first proofs are returned.

II. MANUSCRIPT REQUIREMENTS

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2. The manuscript should be an original typewritten copy (not a carbon). The text must be ready for printing and should be carefully checked for errors. Authors will receive proofs for correction.

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4. Only such references to literature should be given as are referred to in the text. Literature references are to be numbered and listed together at the end of the manuscript and not as footnotes. All references should include the standard (according to the *World List of Scientific Periodicals*) abbreviated title of the journal, year, volume number, and first and last page numbers.

5. The text of articles submitted should be concise and in a readily understandable style. The technical description of the methods used should only be given in detail when such methods are new. The essential contents of each paper should be briefly recapitulated in an abstract in English. Such an abstract may, however, be submitted by the author in the language of the original typescript for translation into English by the editorial staff.

6. To conserve space authors are requested to mark less important portions of the paper (such as description of methods, record of experimental results, etc.) for printing in smaller type.

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by

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